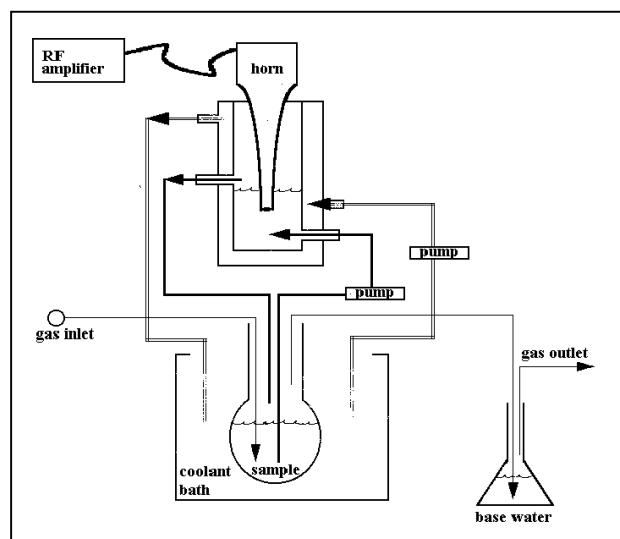




Sonolysis of Nitroaromatic Compounds

1,3-Dinitrobenzene and Nitrobenzene

by Donald M. Cropek and Patricia A. Kemme



The Army generates many unique types of wastes, primarily because of their explosive and toxic characteristics. For example, the production and handling of 2,4,6-trinitrotoluene creates three types of nitroaromatic waste streams. Treatment technologies that serve the private community typically cannot handle them. The variety of these waste streams together with some highly visible problem

areas have stimulated the study of nitroaromatic compound degradation. New chemical treatment methods often involve new methods of producing the highly reactive hydroxyl radical. Since one of the effects of sonolysis on water is the breakdown of water to produce hydroxyl radicals, this work studied sonochemistry as a destruction method for nitroaromatic species in water.

Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers (HQUSACE) under Project 4A161102BT25, “Environmental Research—Corps of Engineers”; Work Unit J88, “Sonolytical Destruction of Nitroaromatic Molecules.”

The work was performed by the Industrial Operations Division (UL-I) of the Utilities and Industrial Operations Laboratory (UL), U.S. Army Construction Engineering Research Laboratories (CERL). The CERL principal investigator was Donald M. Cropek. Walter J. Mikucki was Chief, CECER-UL-I; John T. Bandy was Operations Chief, CECER-UL; and Gary Schanche was the responsible Technical Director, CECER-TD. The CERL technical editor was William J. Wolfe, Technical Resources.

Dr. Michael J. O'Connor is Director of CERL.

Contents

SF 298	Error! Bookmark not defined.
Foreword.....	2
List of Figures and Tables.....	4
1 Introduction.....	7
Background.....	7
Objectives	12
Scope.....	12
Approach	12
Mode of Technology Transfer	12
2 Experimental Parameters.....	14
Chemicals	14
Analytical Equipment	14
Ultrasonic Equipment.....	15
Analytical Sample Preparation.....	17
3 Results and Discussion	18
1,3-Dinitrobenzene (DNB)	18
Sonolysis of DNB.....	19
Nitrobenzene (NB)	22
Future Work	44
4 Conclusions.....	46
References.....	47
Distribution	

List of Figures and Tables

Figures

1	Flow-through sonolysis system operating at 20 kHz.	15
2	Top view of the sonolysis system operating at 660 kHz.	16
3	The structure of DNB.	18
4	LC trace of the original DNB solution before treatment.	19
5	GC/MS trace of the original DNB before treatment.	19
6	LC traces of the DNB solution irradiated at 20 kHz taken at different experiment times. The irradiation time is noted near each trace and the initial DNB solution is shown for comparison.	20
7	Plot of the DNB LC peak area versus irradiation time at 20 kHz.	21
8	The structure of NB.	23
9	LC trace of the original NB solution before treatment. The inset provides an expanded view of the baseline.	23
10	GC/MS trace of the original NB before treatment. The NB peak is observed at 11.1 minutes.	24
11	LC traces of the NB solution irradiated at 20 kHz taken at different experiment times. The irradiation time is noted near each trace and the initial NB solution is shown for comparison.	25
12	Plot of the NB LC peak area versus irradiation time at 20 kHz.	26
13	Plot of TC and TOC of the NB solution and the base water versus irradiation time at 20 kHz.	27
14	GC/MS trace of an ether extract of the treated NB solution after 40 hours of irradiation at 20 kHz.	28
15	GC/MS trace of methylene chloride extract of the treated NB solution after 40 hours of irradiation at 20 kHz.	30
16	GC/MS trace of an ether extract of the base water after 40 hours of irradiation at 20 kHz.	35
17	LC traces of the NB solution irradiated at 660 kHz taken at different experiment times. The irradiation time is noted near each trace and the initial NB solution is shown for comparison.	37
18	GC/MS trace of an ether extract of the treated NB solution after >120 minutes of irradiation at 660 kHz.	38
19	LC trace of the treated NB solution after ether extraction.	41
20	Several additional reactions occurring during sonolysis of NB at 660 kHz.	42

- 21 Mass spectrum of the unknown by-product (peak 16 in figure 18) produced by irradiation at 660 kHz. The inset shows the structure of nitrohydroquinone (MW = 155), which is an identified by-product of photochemical degradation of NB. 44

Tables

- 1 List of peak identifications and structures from the ether extract of the treated NB solution using 20 kHz irradiation. Numbers correspond to the peaks in Figure 14. 28
- 2 List of peak identifications and structures from the methylene chloride extract of the treated NB solution using 20 kHz irradiation. Numbers correspond to the peaks in Figure 15. 30
- 3 List of proposed reactions occurring during sonolysis of NB at 20 kHz. 32
- 4 Analysis of standards by LC. Compounds detected by GC/MS were analyzed by LC; the structure, retention time, and possible peak number in Figure 11 is listed. A value of NB in the Peak Number column indicates probable co-elution with nitrobenzene. 34
- 5 List of peak identifications and structures from the ether extract of the treated NB solution using 660 kHz irradiation. The numbers correspond to the numbered peaks in Figure 18. 38

1 Introduction

Background

The Army generates many types of wastes that are unique, primarily because of their explosive and toxic characteristics. For example, the production and handling of 2,4,6-trinitrotoluene (TNT) creates three types of waste streams. One of these, "yellow water," is primarily composed of acids and is not a high priority problem. The other two waste streams, however, contain TNT as well as other energetic and aromatic compounds, which make them difficult to treat. "Red water" is generated from the purification of TNT to remove the unsymmetrical isomers of TNT. It is classified by the U.S. Environmental Protection Agency (USEPA) as a Resource Conservation and Recovery Act (RCRA) regulated K047 hazardous waste (40 CFR 261, 1996). "Pink water" originates from load, assembly, and packing of munitions, or demilitarization and also contains TNT, as well as two energetic nitramines, HMX and RDX. It is also a RCRA-regulated K047 waste. These two waste streams alone have created an active area of research into treatment technologies for concentrated nitroaromatic waste streams. Treatment technologies that serve the private community typically cannot handle them.

Other types of nitroaromatic species also have energetic characteristics that make them useful for military applications. Dinitrotoluene (DNT) is probably the most common. DNT is used as an ingredient in single-base smokeless powders, military explosives, and ammonium nitrate explosives (Yinon and Zitrin 1993). The USEPA has listed DNT as a hazardous substance. Low effluent permit levels at Army installations have made treatment of DNT a significant concern. Further examples of nitroaromatic compounds include 1,3,5-trinitrobenzene, 2,4,6-trinitrophenol, 2,4,6-trinitrocresol, 2,4,6-trinitroanisole, 2,4,6-trinitroaniline, and 1,3,5-triamino-2,4,6-trinitrobenzene. The large number of different species together with some highly visible problem areas make the study of nitroaromatic compound degradation a valuable and relevant contribution.

A battery of methods exists that have been applied to the treatment of nitroaromatic wastes as well as other Army waste streams. Biological methods

have had some success. For example, an anaerobic fluidized bed reactor has been successfully pilot tested at Radford Army Ammunition Plant for the treatment of DNT wastewater (Maloney et al. 1995). However, biological methods are frequently too sensitive to shock organic loads and are sometimes too chemically specific to be generally useful. Thermal treatment methods such as incineration are not good for dilute streams and currently are not in favor due to their expense and the potential for emitting air pollutants. Chemical treatment methods have generated the greatest amount of research interest. These methods can be effective, but are frequently plagued by inefficiencies due to slow kinetics or mass transfer problems. With any of these techniques, complete mineralization of the organic contaminant is difficult to achieve, and transformation products are sometimes as problematic as the initial material.

Chemical methods fall into two main categories, oxidation and reduction. Although the nitro group is already in its highest oxidation state, processes that reduce the nitro group are surprisingly uncommon. One example of this type of work is electrochemical reduction — currently being studied by the U.S. Army Construction Engineering Research Laboratories (CERL). Mineralization or transformation of the nitroaromatic molecule by oxidation is far more frequent. Wet air oxidation, supercritical water oxidation, UV/H₂O₂, UV/ozone, and Fenton's reagent are typical oxidation methods. In each of these processes, the hydroxyl radical is the active agent that indiscriminately attacks the organic contaminant. Complete mineralization of the organic compound into innocuous by-products such as carbon dioxide, water, and inorganic nitrogen species is usually the desired goal. New treatment methods often involve new methods of producing the hydroxyl radical. Since one of the effects of sonolysis on aqueous solutions is the breakdown of water to produce hydroxyl radicals, this work studied the potential of sonochemistry as a treatment method for organic constituents in water.

Sonochemistry

Sonochemistry is defined as the chemical effects produced by subjecting a chemical reaction to sound waves (Bremner 1990). Ultrasound, with frequencies roughly between 15 kHz and 10 MHz, has a drastic effect on chemical reactions. The mechanism that causes this effect is known as "acoustic cavitation." This phenomenon proceeds as follows. A sound wave impinging on a solution is merely a cyclic succession of compression and expansion phases imparted by mechanical vibration. During the solution expansion phase, small vapor-filled bubbles are formed due to weak points in the solution, primarily at trapped gas pockets on particulate surfaces. These bubbles grow and contract in response to

the expansion and compression phases of the cycle, respectively. Because the surface area of the bubble is greater during the expansion phase than during the compression phase, growth of the bubble is greater than the contraction, resulting in an increase in the average bubble size over many cycles. Over time, the bubble reaches a critical size depending on the ultrasonic frequency, whereupon the pressure of the vapor within the bubble cannot withstand the external pressure of the surrounding solution. The result is a catastrophic collapse of the bubble with high velocity jets of solution shooting into the interior. This implosion process is known as acoustic cavitation. Extreme environments are produced in and near the bubble as a result. Suslick (1989 and 1990) gives a more detailed explanation of acoustic cavitation.

Although many bubbles are produced, these bubbles are quite small. It is estimated that 4×10^8 bubbles/second/ m^3 are produced (Suslick and Hammerton 1986). The bubbles are on the order of 10 to 200 microns in diameter, and they are short lived, with a lifetime near 10 microseconds. Therefore, the bulk solution conditions remain relatively unaffected. But the implosion of the bubble causes enormous local effects. The temperature of the vapor within the bubble has been estimated to reach as high as 5000 °K (Suslick, Cline, and Hammerton 1986) with a concomitant pressure near 1000 atm (Mason and Lorimer 1988). The principal result of these conditions in an aqueous solution is the breakdown of water vapor in the bubble into hydrogen and hydroxyl radicals. This essentially transforms the bubble into a microreactor where interesting chemistry can occur.

Uses of Sonochemistry

The unusual microenvironments created during acoustic cavitation permit a wide variety of uses for ultrasound. These uses include homogenization and cell disruption in the biological field, dissolution and mixing in chemistry, soldering and welding in metal working, degreasing and emulsification in industry, and polymerization and depolymerization (Bremner 1990). Novel chemical applications result from the catalytic effects of sonochemistry. This includes the creation of new compounds, for example, new iron carbonyl compounds (Suslick et al. 1991), new and more effective catalysts (Suslick and Casadonte 1987), and greater rates and yields on chemical reactions (Luche 1990). Research areas such as these provide the majority of sonolytic applications. In the past several years, the use of sonochemistry as a destruction technique has blossomed.

Applying ultrasound to an aqueous system initiates the cavitation process. If organic species are also present in the water, it is expected that degradation will occur, ultimately to complete mineralization. The extreme conditions created by

acoustic cavitation initiate three distinct destruction pathways for organic contaminants: oxidation by hydroxyl radicals, supercritical water oxidation, and pyrolysis. It has been proposed that pyrolytic mechanisms dominate at high solute concentrations while hydroxyl radical attack dominates at low solute concentrations (Kotronarou, Mills, and Hoffmann 1991).

The primary mechanism is hydroxyl radical oxidation. The severe conditions are enough to break down water vapor within the bubble into hydrogen and hydroxyl radicals. But the highly reactive nature of these radicals prevents a long travel pathlength into the solution. Therefore, only organic molecules present within the bubble or very near the bubble surface will be destroyed in this fashion. Note the simultaneous production of the hydrogen radical indicates that reductive pathways may also be available for organic breakdown.

Supercritical water is a phase of water that exists above its critical temperature and pressure, 647 °K and 221 atm. This unique state of water has different density, viscosity, and ionic strength properties than water under ambient conditions. Supercritical water oxidation (SCWO) is one technique studied for the treatment of contaminants in wastewater (e.g., Harradine et al. 1993). Since the organic contaminant has an increased solubility within supercritical water, these organic species are brought into close proximity with the oxidant, usually oxygen from dissolved air. Oxidation is therefore accelerated. During sonolysis, it is proposed that supercritical water is present in a small thin shell around the bubble (Hoffmann, Hua, and Hochemer 1996). According to these researchers, this mode of destruction is expected to be secondary in importance because the fraction of water in the supercritical state is estimated to be on the order of 0.0015 parts out of 100 parts of water. Alternatively, the volume of the gaseous bubble is estimated to be 2×10^4 times greater than the volume of the thin supercritical water shell surrounding the bubble. The value of supercritical water may be limited to increasing the solubility of the organic contaminant near the bubble interface for radical attack. The possible occurrence of SCWO in the sonochemical reactor, however, may be one reason to justify the use of an oxygen-containing purge gas.

A third mechanism is pyrolytic breakdown of organic contaminants. Pyrolysis is defined as the thermal destruction of a compound in the absence of oxygen. The high temperatures attained within the bubbles are well above the temperatures required to destroy organic materials. This mechanism, however, requires the compound to be present in the vapor phase within the bubble. Compounds with higher vapor pressures will have a higher vapor concentration inside the bubble.

It is expected then that pyrolysis will be more prevalent as the vapor pressure of the contaminant increases.

The above mentioned conditions created in the bubble during collapse would clearly degrade organic species present within the bubble interior. But since bubble implosion occurs by the influx of a jet stream of the surrounding liquid, it may not be necessary for the organic contaminants to be initially present in the bubble interior for degradation to occur. This implosion scenario is analogous to the injection of contaminated liquid directly into the hot reaction zone.

Ultrasonic Degradation

Several researchers have already experimented with the use of ultrasound for the express purpose of degradation of organic contaminants. Nearly all are performed in aqueous media for relevance to treating contaminated ecosystems. Chlorinated compounds such as carbon tetrachloride (Francony and Petrier 1996), trichloroethylene (Drijvers et al. 1996), chloroform (Petrier, Reyman, and Luche 1995), pentachlorophenate (Petrier et al. 1992), methylene chloride (Cheung, Bhatnagar, and Jansen 1991), and chlorofluorocarbons (Hirai, Nagata, and Maeda 1996) seem to be the most studied class of compounds. Most of these species have a high vapor pressure and tend to concentrate within the bubbles allowing fast degradation down to chlorine ions, CO₂ and other inorganic species. It is concluded that the degradation mechanism is pyrolysis rather than hydroxyl radical attack.

Phenolic compounds have also been studied. These compounds provide a more opportune system because of their relatively high solubility in water. Therefore, volatility is a lesser concern than with other contaminants. Sonolysis of phenol (Petrier et al. 1994; Serpone et al. 1982) showed mineralization of phenol with benzoquinone, hydroquinone, and catechol as the organic intermediates and oxalic, maleic, acetic, formic, and propanoic acids as the short chain polar intermediates (Berlan et al. 1994). Other similar species include methyl phenols, hydroxyanisoles, resorcinol (Takizawa et al. 1996) and chlorophenols (Serpone et al. 1994). All are degraded by hydroxyl radical attack.

The sonolytic degradation of other chemical species includes dextran (Lorimer et al. 1995), sodium hypochlorite (Mason et al. 1996), iodide and bromide (Gutierrez, Henglein, and Ibanez 1991), arylalkanes (Soudagar and Samant 1995), and glyceraldehyde (Fuchs and Heusinger 1995).

Nitro compounds are of special interest. Sonochemical reactions of nitrotoluenes in the presence of potassium permanganate oxidize the -CH₃ group to -COOH

(Soudagar and Samant 1995). p-Nitrophenol degrades primarily by denitration during pyrolysis with radical attack of minor importance to produce NO_2^- , NO_3^- , benzoquinone, hydroquinone, 4-nitrocatechol, formate, and oxalate (Kotronarou, Mills, and Hoffmann 1991). Sonolytic by-products from TNT have been studied. The proposed first step is hydroxyl radical attack on the methyl group to form 2,4,6-trinitrobenzoic acid. Other products include trinitrobenzene, hydroxylated TNT derivatives, acetate, formate, glycolate, oxalate, CO_2 , NO_3^- , and NO_2^- (Hoffman, Hua, and Hochemer 1996).

Objectives

The objectives of this study were to: (1) study of the rate of disappearance of the initial nitro species when subjected to sonolysis (the focal point) and (2) monitor and identify the appearance of by-products (to contribute to a more complete understanding of the degradation mechanism).

Scope

This work did not focus on increasing the reaction rate of disappearance of the initial nitro species, but instead noted the experimental parameters that either positively or negatively affected the rate.

Approach

Nitrobenzene and dinitrobenzene were selected as the initial model compounds for their simplicity and relatively safe handling. Aqueous solutions of these two species were sonolytically treated under two different frequency conditions. Instrumentation for monitoring the progress of degradation included one or more of the following: a total organic carbon instrument, a liquid chromatograph with a UV/Visible absorbance detector, and a gas chromatograph/mass spectrometer.

Mode of Technology Transfer

It is anticipated that the results of this study will provide information and direction for applied research on the use of sonolysis to treat nitroaromatic containing wastes. Specifically, the results of this work will apply to compliance, pollution prevention, remediation, and demilitarization of aqueous waste

streams containing nitrocompounds. Because of its nonspecificity, sonolysis may also provide an additional method to treat other recalcitrant waste streams.

2 Experimental Parameters

Chemicals

Dinitrobenzene (Aldrich, 97 percent) and nitrobenzene (Sigma, 99.9 percent) were used as received. The acetonitrile used as a mobile phase solvent for liquid chromatography (LC) was HPLC grade (Fisher). Extractions were performed with either ether (Aldrich, 99.8 percent anhydrous) or methylene chloride (Fisher, HPLC-GC/MS grade). All water used for either a mobile phase component or during preparation of the solution to be sonicated was distilled and deionized with a Milli-Q Plus system (Millipore Systems). When preparing the LC mobile phase, both the water and acetonitrile were filtered with a 0.45 μm pore size nylon filter (Micron Separation Inc.).

Analytical Equipment

A Dohrmann DC-80 Total Organic Carbon (TOC) Analyzer was sometimes used to follow the course of the reaction. A solution of potassium persulfate (Sigma) with phosphoric acid (Fisher, HPLC grade) was used as the TOC internal solution. Potassium hydrogen phthalate (Fisher, A.C.S) was the carbon standard.

The progress of sonolysis was monitored by high performance liquid chromatography (HPLC) using a Waters Associates liquid chromatograph (LC Module Plus 1) consisting of a Model 600 HPLC pump and a Model 486 UV/Visible absorbance detector. The detection wavelength was 254 nm and the LC column was an ABZ+ column, 25 cm x 4.6 mm, with a 5 μm diameter particle size (Supelco). In all cases, the mobile phase was a water-acetonitrile mixture (70:30) with a flow rate of 2.0 mL/minute and an injection volume of 10 μL .

A Hewlett-Packard Gas Chromatograph/Mass Spectrometer (GC/MS) system consisting of a 5890 GC, a 5970 mass sensitive detector, and the G1034C Chem Station operating software was used for the identification of by-products. The column was a HP Ultra 2 capillary column, 25 m x 0.2 mm, with a 0.33 μm film thickness coating of cross-linked 5 percent phenyl/95 percent methyl silicone.

The GC method set the injector and detector port temperatures at 250 and 280 °C, respectively. The GC injector was operated in the splitless mode. The GC oven temperature program was held initially at 40 °C for 10 minutes, then was ramped at 10 °C/minute to 250 °C and held for 4 minutes. The total acquisition period was 35 minutes. The mass analyzer was set to scan from 10 to 350 amu.

Ultrasonic Equipment

The ultrasonic irradiation of aqueous solutions was performed using two different systems. The first was a Vibracell Model 600 direct immersion ultrasonic horn (Sonics and Materials) that was operated at 20 kHz with a maximum power output of 600 watts/cm². Figure 1 shows the experimental arrangement. The bulk sample solution was pumped into the reaction chamber at approximately 1.0 mL/minute and recirculated back down into the bulk vessel. Both the reaction chamber and the bulk solution vessel are maintained at a constant temperature by the coolant bath (Grant Instruments).

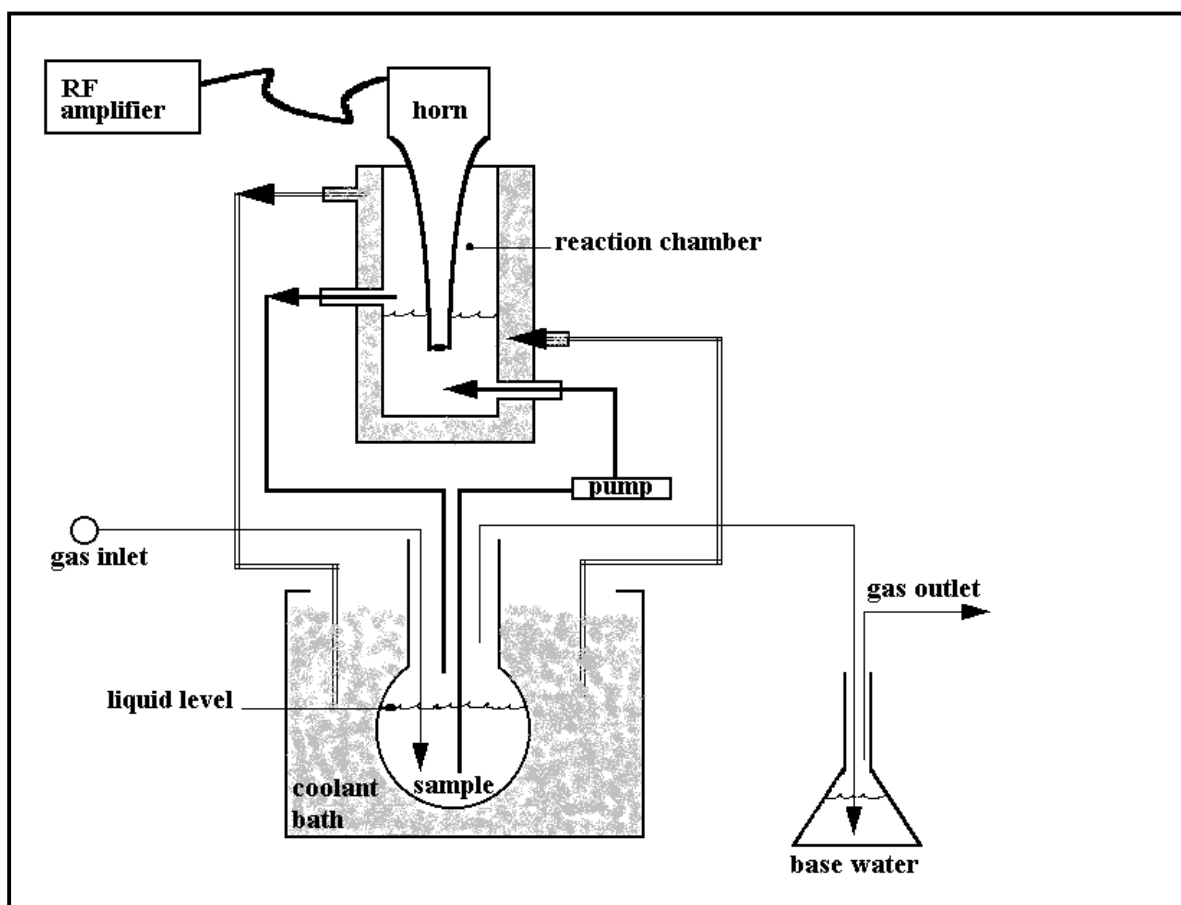


Figure 1. Flow-through sonolysis system operating at 20 kHz.

The ultrasonic horn was submerged in the solution and made an airtight seal with the reaction chamber. Compressed air was sparged continuously into the bulk solution via the gas inlet line. The gas outlet line from the bulk solution was submerged into an alkaline water solution (pH > 12) to capture carbon dioxide evolving from the sonolysis reaction. This alkaline solution also served to partially capture volatile organic components from the reaction. The sample solution in the reaction chamber was then continuously irradiated at an amplitude setting of 50 percent.

The second system used a transducer system operating at 660 kHz with a power output between 240 and 960 watts (Ultrasonic Energy Systems). Figure 2 shows this setup. Several items are numbered for easy reference. A specially designed jacketed vessel made by Ace Glass was affixed to the transducer plate using Dow Corning silicone sealant (see No. 1 in Figure 2). Items numbered 2 through 10 are ports that open into the vessel; ports numbered 7 through 10 are along the top of the vessel. The reaction vessel was filled with the solution to be sonicated; a volume of approximately 750 mL. The sound waves traverse the length of the vessel in a plane wave (as shown, the sound waves travel from left to right), hit the concave end of the vessel, and are reflected back to a focal point located just below the port No. 10. The vessel can be temperature controlled by flowing a thermostated solution into port No. 2 and out port No. 3.

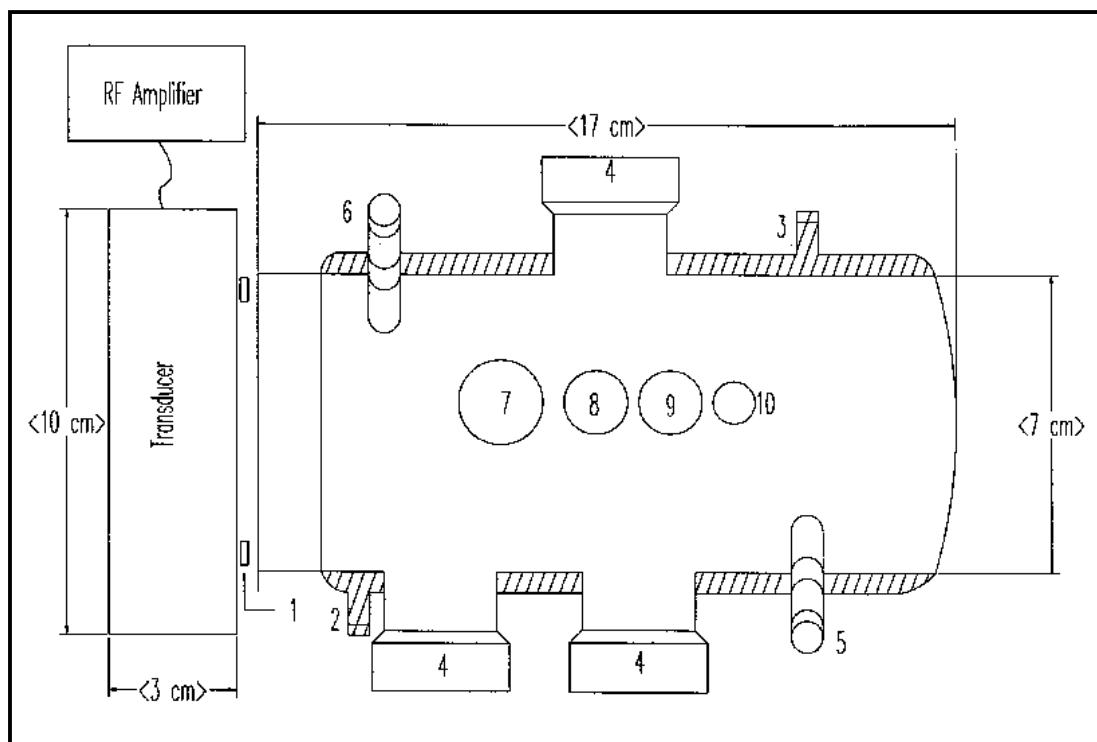


Figure 2. Top view of the sonolysis system operating at 660 kHz.

Ports No. 8 and No. 9 are for gas purging but in these experiments, they were left open to ambient air. Port No. 6 is for insertion of a thermometer and port No. 7 can accommodate a pH electrode. Port No. 5 is currently an excess port. Samples can be taken from port No. 10, which is designed primarily to take samples from the focal point during sonication. Three large windows in the side of the vessel labeled No. 4, complete with quartz windows for optical interrogation of the reaction, are available if required. The vessel was cooled to 7 °C during these experiments. The solution was then irradiated with sound waves having a pulse width and repetition rate settings of 2.0 and an amplitude of 6. These settings result in a pulsed irradiation of 0.25 seconds on and 2.8 seconds off. The actual irradiation time in seconds can be calculated by multiplying the total instrument on-time in minutes by 4.83.

Analytical Sample Preparation

One to two mL samples were taken from a reaction vessel and filtered through a Gelman PVDF filter (0.45 µm pore size) before analysis. This was primarily for removal of titanium metal particulates produced during sonication via erosion of the titanium tip of the 20 kHz horn. These filtered samples are immediately amenable for analysis by either LC or TOC. When GC/MS analysis was required, a solvent extraction with either ether or methylene chloride was performed immediately after samples were taken. For complete extraction, the aqueous sample was washed three successive times with the organic solvent using a 1:3 volume ratio of organic solvent to aqueous solution. These three organic washes were combined and concentrated by a Zymark Turbo Vap Concentrator to a final volume of 1 mL. This concentrated solution was then analyzed by GC/MS via direct injection.

3 Results and Discussion

1,3-Dinitrobenzene (DNB)

Figure 3 shows the structure of DNB. This molecule was chosen for initial experiments in sonolytic degradation in an aqueous solution. Due to its well nitrated, aromatic structure, DNB was believed to be a good choice as a model compound for the highly nitrated, energetic compounds to be studied later. One problem, however, is its low solubility in water. According to Lange's *Handbook of Chemistry* (Dean 1972), DNB has a solubility of about 0.05 grams per 100 grams of water, or a limit of 500 ppm. A solution of DNB in water was made by oversaturating the solution with DNB and decanting the required amount of solution from this. This solution is directly injectable into the LC. Figure 4 shows the chromatogram of DNB. The retention time is 9.4 minutes with a peak area of 8.78×10^6 . A calibration curve of LC peak area versus DNB concentration was created using solutions of DNB dissolved in a 70 percent water/30 percent acetonitrile mixture. Based on this calibration data, the initial solution of DNB is calculated to be 177 ppm or 1.05 mM.

The inset of Figure 4 shows the enhanced baseline of the LC trace of DNB in water. The injection peak at 1.6 minutes is common to all LC chromatograms. Note the several small peaks due to minute impurities in the DNB. Based on the retention time, these species are not ionic, otherwise they would appear very close to the injection peak. Furthermore, detection at 254 nm implies that these species are unsaturated and most likely aromatic in nature. A sample of the DNB was dissolved in methylene chloride and analyzed by GC/MS. Figure 5 shows this chromatogram. The large peak at 19.1 minutes is DNB, but all remaining peaks are due to silanes from column bleed. No evidence of contaminants was noted by GC/MS. No further efforts were made to identify the contaminants observed by LC.

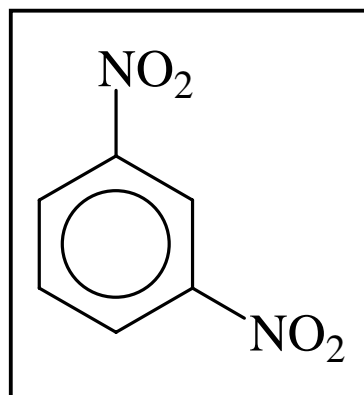


Figure 3. The structure of DNB.

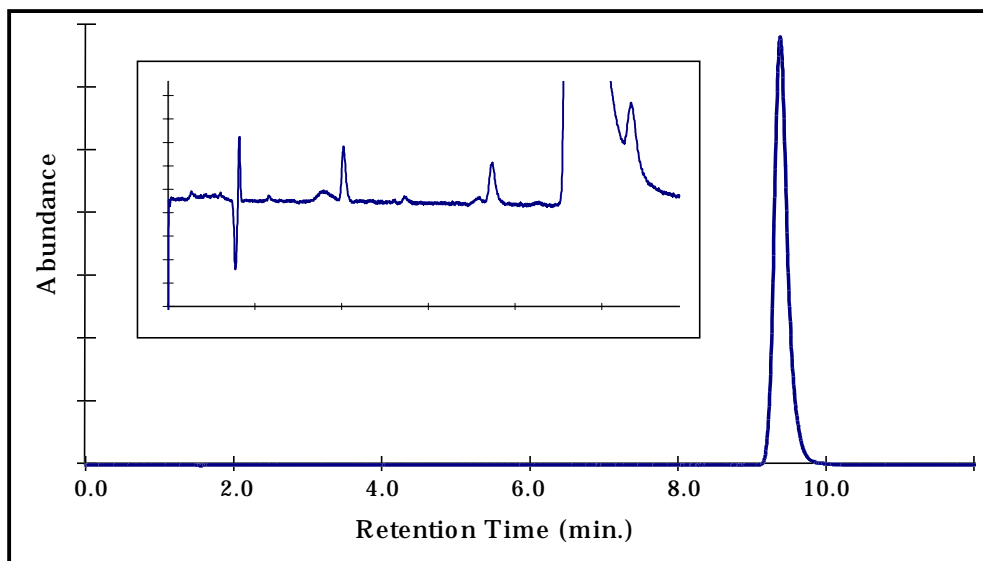


Figure 4. LC trace of the original DNB solution before treatment.

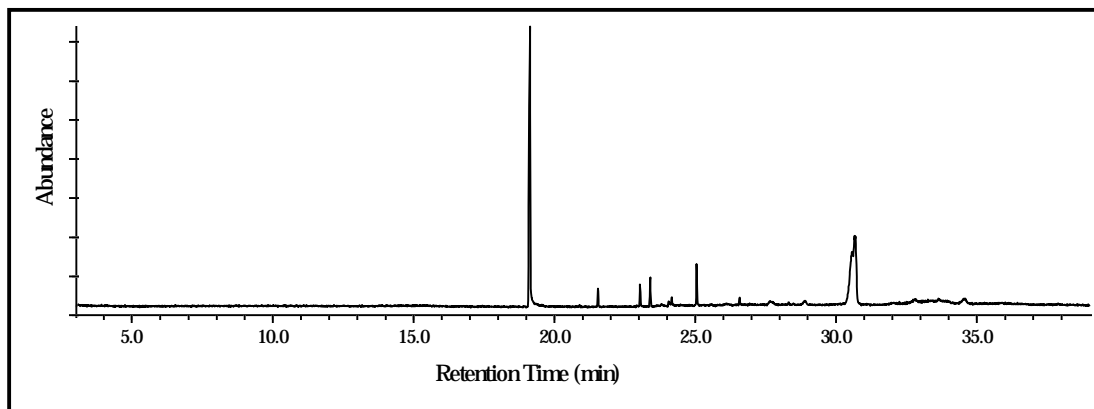


Figure 5. GC/MS trace of the original DNB before treatment.

Sonolysis of DNB

With the flow-through system described in the experimental section (Figure 1), but without the base water vessel, sonolysis on DNB was performed with 20 kHz irradiation. No aeration was performed, but this system has a long flow path and is not completely air tight, so complete degassing of the DNB solution does not occur. The bulk solution vessel and the sonolysis chamber were both chilled to 5 – 7 °C. The experiment was irradiated for 1-hour time periods after which a small sample was taken for LC analysis. Figure 6 shows the chromatograms from this experiment. The initial LC trace is also shown for comparison. The baseline has been expanded for observation of the small by-products and an offset in the y-direction has been added to each for clarity.

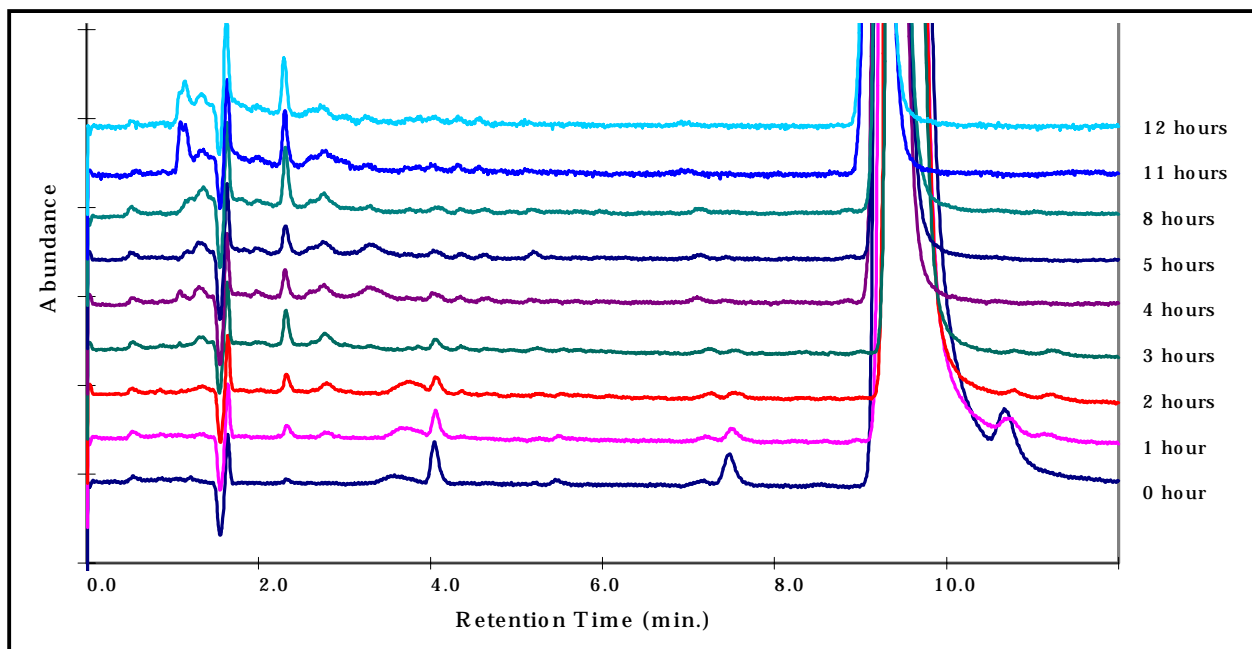


Figure 6. LC traces of the DNB solution irradiated at 20 kHz taken at different experiment times. The irradiation time is noted near each trace and the initial DNB solution is shown for comparison.

After only 1 hour, several characteristics appeared that extend throughout the experiment. First, the baseline peak width of the DNB peak was drastically reduced indicating a reduction in the DNB concentration. This will be discussed further below. The second obvious change was the quick degradation of the impurities. The largest impurity at 10.7 minutes that contributes to the DNB peak width was completely eliminated after 2 hours of irradiation. The other impurities were either more stable or do not readily enter the active cavitation regions. These compounds were degraded by the fourth hour of reaction time.

The third change was the growth of by-products as the DNB is degraded. Since the sonolytic destruction process is not a single step process to gaseous by-products, the presence of by-products is essential to prove that the disappearance of DNB is not merely volatilization. The first peak immediately present after 1 hour of irradiation is the small peak, at 2.3 minutes. Notice that this peak is already present in the initial DNB solution, although quite small. It is the major by-product at all reaction times. It is not certain whether sonolysis of DNB or sonolysis of the impurities is the source of this by-product. This peak does not grow from 8 to 12 hours of irradiation; this seems to correlate with the loss of all impurities. Another portion of the chromatogram that changes is near the injection peak. At later reaction times (>4 hours), numerous by-products are produced in small concentrations as evidenced by the small broad peaks occurring from 1.0 to 1.5 minutes.

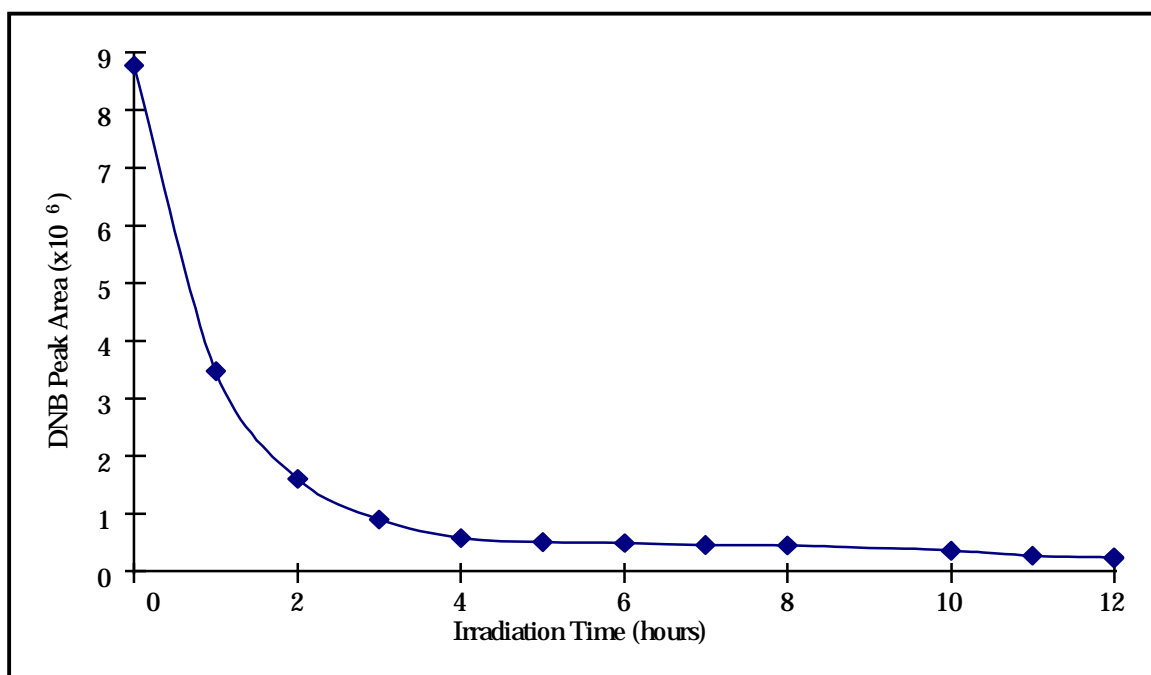


Figure 7. Plot of the DNB LC peak area versus irradiation time at 20 kHz.

The disappearance rate of DNB can be obtained by measuring the DNB peak area over time. Figure 7 shows the plot of the DNB peak area versus irradiation time. The data in this figure indicate two different rates. From zero to 4 hours, the disappearance rate is fast. In the first hour alone, the DNB concentration is reduced by over 60 percent. The disappearance rate, however, begins to slow and after 4 hours, there is only a negligible decrease with every additional hour of sonication.

Discussion

Comments can now be made on the degradation of DNB. The dramatic drop in DNB concentration after only 1 hour of irradiation should have been accompanied by a rise in the variety and abundance of by-products. Since this was not the case, may be that the loss of DNB is not sonolytic breakdown but is instead ultrasonically assisted volatilization. The agitation produced during irradiation stimulates the loss of this nonsoluble organic compound. In addition, the experimental arrangement provides a great deal of surface area, which helps increase volatilization. By-products slowly increase over time, indicating that sonolytic destruction does occur, but that it is only a minor factor for DNB loss.

By the end of the 12-hour experiment (Figure 6), the solution was gray in appearance with a black precipitate. Examination of the titanium tip of the horn showed a great deal of erosive pitting and wormholing. The solution particulate

was due to the mechanical degradation of the vibrating horn tip. Since the propagation of the sound waves into the solution is directly related to the smoothness of the tip, the tip was changed after the twelfth hour and two additional 1-hour irradiation experiments were performed. Irradiation with the new tip resulted in the DNB concentration dropping from 4 ppm after the twelfth hour to 3 ppm and 2 ppm after hours 13 and 14, respectively. This insignificant DNB loss with the new tip indicates that the slowing of the DNB loss rate noted in Figure 7 is not due to inefficient transfer of energy into the solution, but instead is due to a decrease in the volatilization rate.

After 14 hours of irradiation, an aliquot of the original DNB solution was added to the experimental solution. Analysis by LC indicated that the new concentration of DNB was 102 ppm. After 1 more hour of irradiation (15 total hours of irradiation), the DNB concentration dropped to 66 ppm. This was similar to the first hour shown on Figure 7 when the large DNB concentration quickly dropped. Therefore, the system behavior was consistent and the lack of by-products pointed to DNB volatilization rather than a sonolytic destruction mechanism.

Due to an instrument failure, none of these DNB samples were studied by GC/MS. Nevertheless, the abundance of the by-products, as seen by LC, may be too low for useful mass spectral analysis and the expected polar character of these by-products may prevent adequate solvent extraction by ether. From other experiments, however, some suggestions may be made regarding the identification of by-products in Figure 6. 1,4-Benzoquinone is a typical intermediate of oxidation reactions; this compound has a retention time of 2.3 minutes, suggesting this as a likely candidate for the major DNB by-product at this same retention time in Figure 6. The species that elute near the injection peak (1.0 – 1.5 minutes) prefer to partition into the mobile phase and have essentially no retention on this stationary phase. These compounds are hydrophilic or even polar in character. Organic ion intermediates such as formate, acetate, or oxalate are quite possibly the compounds causing these peaks.

Nitrobenzene (NB)

Figure 8 shows the structure of NB. This molecule is the simplest nitroaromatic molecule and may provide easily interpretable data on the degradation mechanism. NB has a better solubility in water at 1900 mg/L than DNB (Dean 1972), but it is still difficult to dissolve. A bulk solution of approximately 200 ppm (1.62 mM) NB in water was used for degradation experiments. This solution can be directly analyzed by LC.

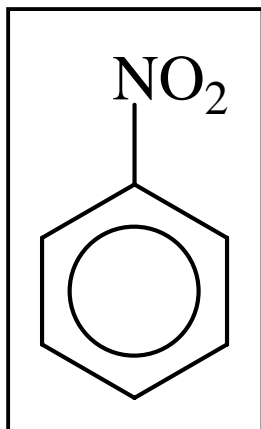
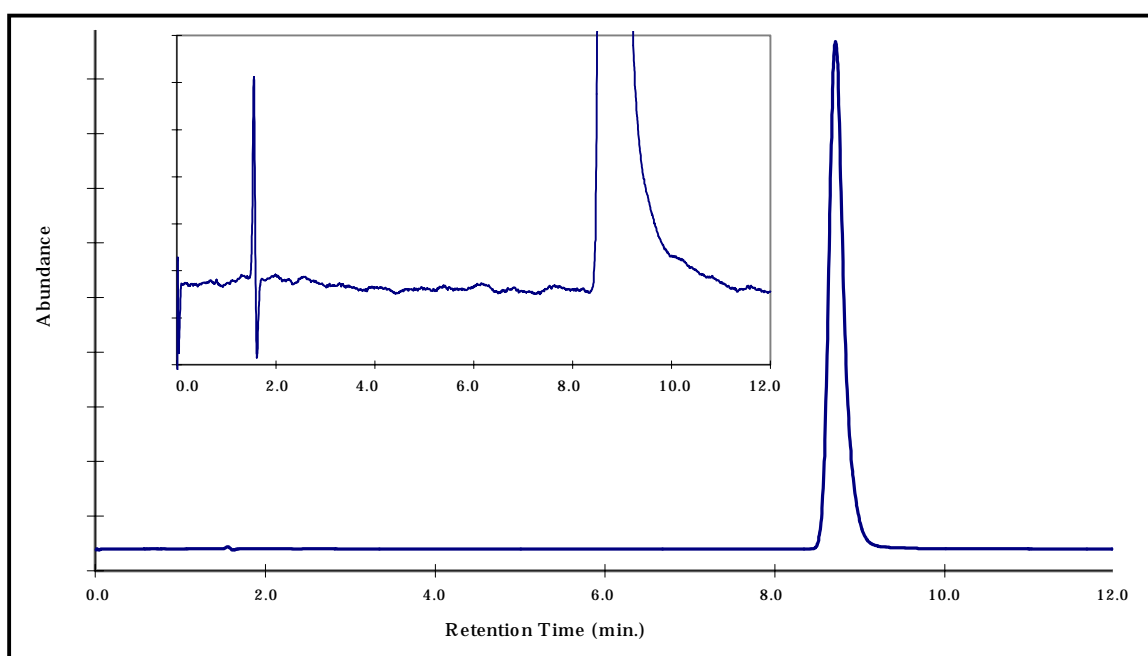


Figure 8. The



structure of NB.

Figure 9. LC trace of the original NB solution before treatment. The inset provides an expanded view of the baseline.

Figure 9 shows the chromatogram of NB. The inset of Figure 9 shows the expanded baseline. Unlike the DNB solution, the NB solution has no discernable contaminants. The retention time was 8.7 minutes with a peak area of 2.04×10^6 .

A solution of NB in methylene chloride was also analyzed by GC/MS. Figure 10 shows the chromatogram of NB. The inset in Figure 10 shows the expanded baseline. Only the large NB is seen at 11.1 minutes. This GC/MS data supports the LC data on the purity of the NB.

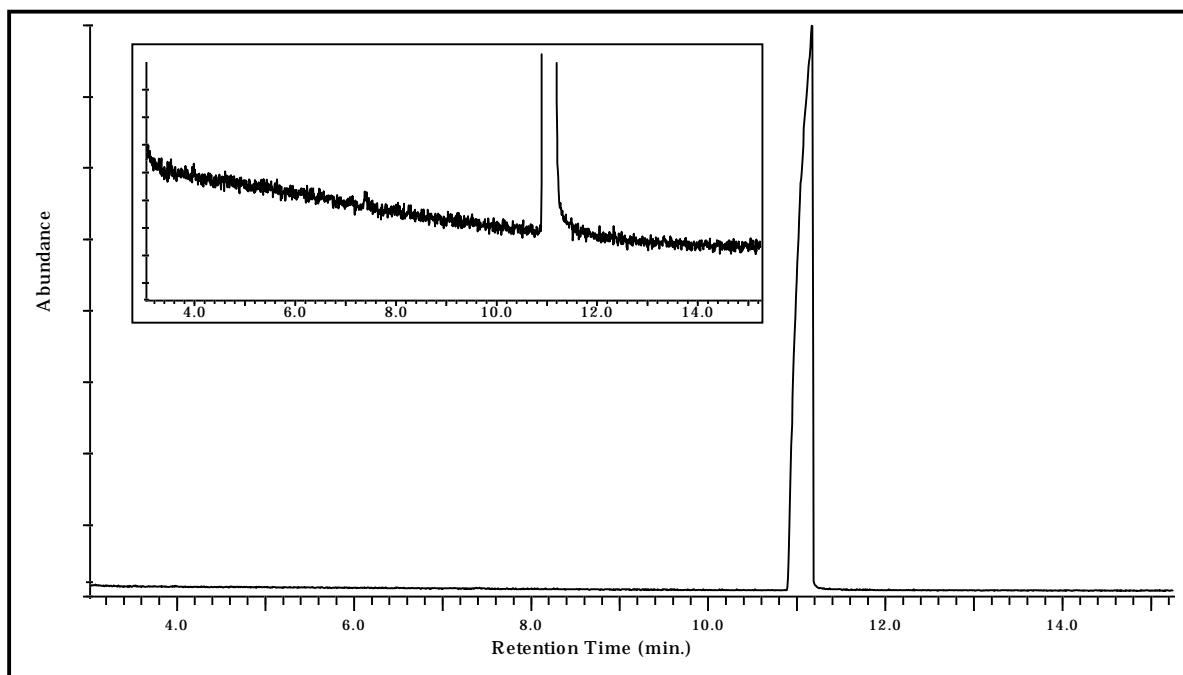


Figure 10. GC/MS trace of the original NB before treatment. The NB peak is observed at 11.1 minutes.

Sonolysis of NB - 20 kHz

Sonolysis on NB was performed with the flow-through system and the horn operating at 20 kHz. The system was bubbled with compressed air to ensure that the solution was well aerated during the experiment. The base water vessel was in place to catch escaping gases. This would also increase concerns regarding volatilization of the NB. The bulk solution vessel and the sonolysis chamber were maintained at 20 °C. The experiment was irradiated for 1-hour time periods after which a small sample was taken for LC analysis.

The progress of this experiment was gauged by monitoring the LC data. Figure 11 shows chromatograms from this experiment. The peaks are numbered according to increasing retention time. The first observation is the shifting retention times over the 20-day course of this experiment. The peak shift is most notable for NB (peak 13). The NB retention time is 8.7 minutes for the zero hour experiment; it moves to a shorter time for the 1- through 10-hour experiments, then shifts back to 8.7 minutes for the 20- and 40-hour runs. This could be due to a change in pH since the mobile phase is not buffered, but this retention shift is most likely due to a drift in temperature of the LC system. The shift of most of the peaks is easy to follow. After 1 hour of irradiation, by-product peaks are already present and are more numerous than by-products observed from DNB

degradation. Peaks 2, 3, 5, 7, 9, 11, and 12 steadily grow in size from 1 to 4 hours with no new peaks appearing.

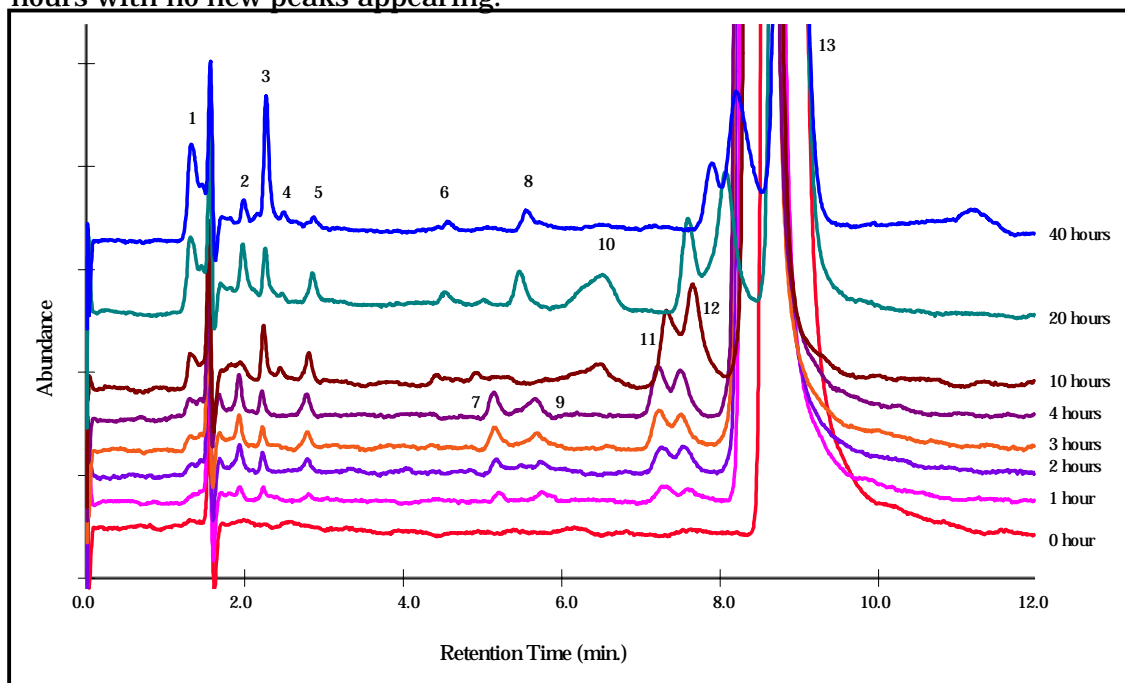


Figure 11. LC traces of the NB solution irradiated at 20 kHz taken at different experiment times. The irradiation time is noted near each trace and the initial NB solution is shown for comparison.

This indicates that these are the stable sonolytic by-products from NB degradation. If the solution continues to be irradiated in this manner, the breakdown of NB will continue to occur in this fashion. This experiment, however, was stopped at various times including overnight, weekend, and during instrument down time. During these inactive times, the solution components change. These changes are noted by LC, as shown in the chromatogram for hour 10. Peaks 2, 7, and 9 are gone while peaks 1, 4, and 10 appear. It is not certain whether the missing species have volatilized or have been further degraded over time in a kind of “dark” reaction. The 20-hour chromatogram shows the reappearance of peak 2, new peaks 6 and 8, and the continued presence of peaks 4 and 10. The last chromatogram at 40 hours of irradiation has been stopped and started many times and has primarily peaks 1, 2, 3, 8, 11, and 12. The large peaks 3, 11, and 12 remain a constant presence throughout the runs. The changing characteristics of the LC indicates that for consistent data, downtime must be minimized. Peak 1 elutes before the injection peak, indicating that it travels through the column faster than the water solvent. This behavior points to a very polar or ionic compound since it is attracted more to the mobile phase than to the stationary phase. The appreciable absorbance at 254 nm means that it has some unsaturation. It is likely a larger molecule able to bypass many of the pores in the column. This decreases the tortuosity of its path thus giving it a shorter average pathlength than water. Peaks with these elution characteristics

may also be organic ions such as acetate or propionate created during the pathway to carbon dioxide.

The peak area of the NB was monitored over the course of this experiment. The plot in Figure 12 indicates the loss of NB over time. The loss of NB is clearly slower than the loss of DNB noted in Figure 7. The difference, however, is that the simultaneous production of by-products from NB points to actual sonolytic destruction rather than just volatile loss as seen for DNB. Some NB loss to the gaseous phase is still expected. Figure 12 clearly shows two different loss rates with the break between the two occurring at about 12 hours. It is hypothesized that the faster rate of NB disappearance at the earlier time is a combination of a large rate of volatilization and a small rate of sonolysis while the later, slower rate of NB disappearance is primarily due to sonolysis.

Figure 13 shows a plot of the total carbon (TC) analysis for this experiment. The carbon analysis of the NB solution shows a drop in both TC and TOC while analysis of the base water shows a simultaneous rise in both TC and TOC over the course of the experiment. The initial TC value for the NB solution is 103 ppm which correlates to an initial NB concentration of 176 ppm. From this initial value, TC drops linearly until the tenth hour when a decrease in the slope is again observed for the remainder of the experiment. TOC values illustrate the same behavior with a 40 percent decrease in the first hour. The difference between TC and TOC is the value of total inorganic carbon (TIC) present in the solution, usually in the form of carbonates or bicarbonates.

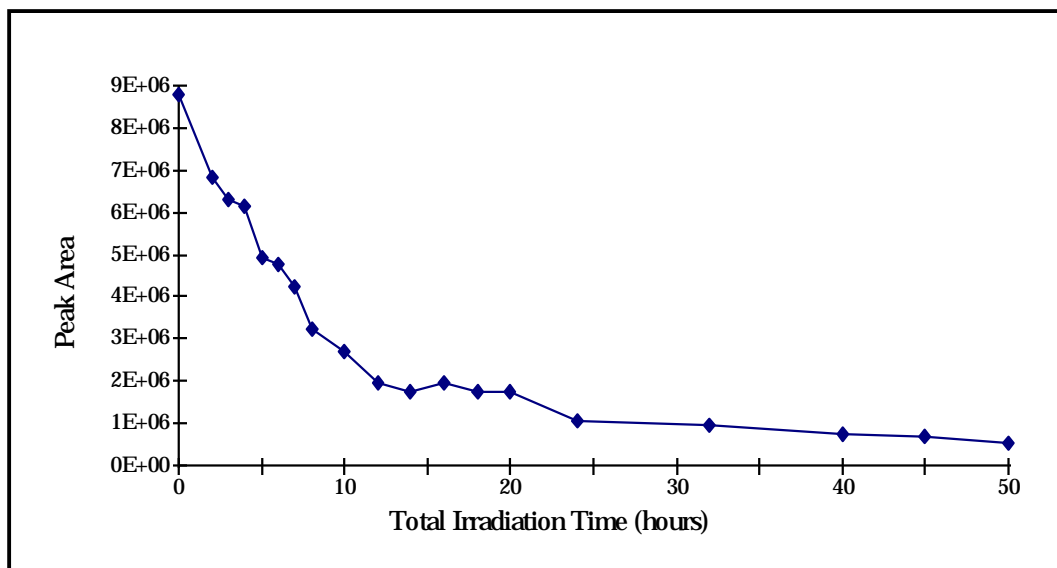


Figure 12. Plot of the NB LC peak area versus irradiation time at 20 kHz.

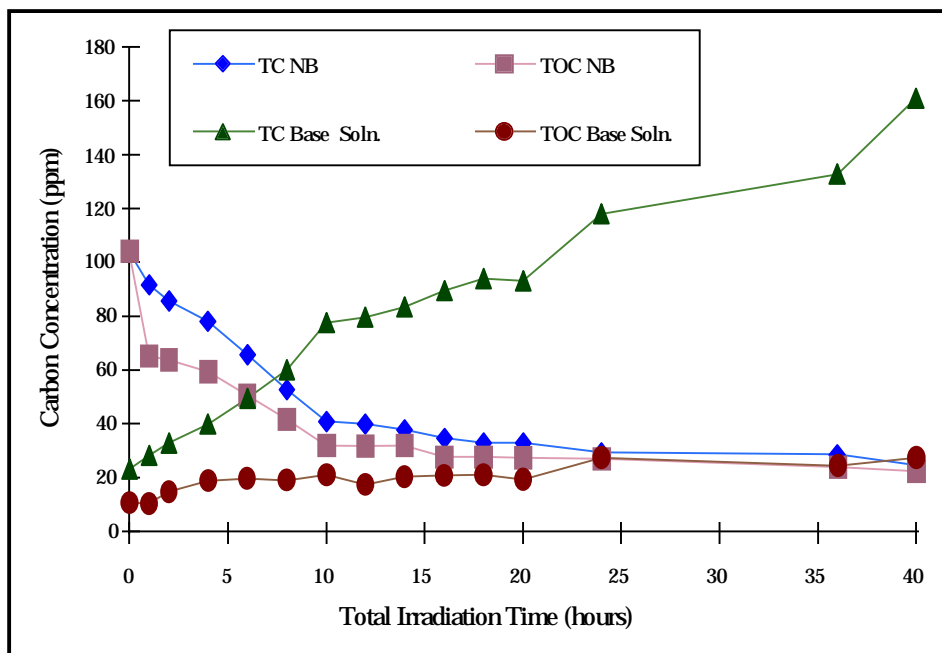


Figure 13. Plot of TC and TOC of the NB solution and the base water versus irradiation time at 20 kHz.

Information on the off-gases from this experiment is obtained by TC and TOC analysis of the base water. This alkaline solution will convert any CO_2 that bubbles through it into carbonate, CO_3^{2-} . Organic compounds that escape the system may also be slightly trapped, but use of this system to measure organics is limited since only hydrophobic species are expected to escape; this base water is constantly sparged by the system gas. From an initial value of 23 ppm, TC rises to a value of 160 ppm after 40 hours. In an airtight system, TC of the base water should not increase above 23 ppm (initial value) + 103 ppm = 126 ppm if all the TOC from the NB solution is converted to CO_2 . This indicates that either the purge air contains some amount of CO_2 or that leaks in the system allow ambient CO_2 to enter the system. Since the value of TOC for the base water slowly increases from 10 ppm to 29 ppm over the course of the experiment, some organic material from the reaction system is escaping.

At the end of the above experiment, an aliquot of the treated NB solution was taken for GC/MS analysis. An extraction with ether was taken, concentrated, and a 2 μl injection of the extraction was analyzed. Figure 14 shows the chromatogram of this sample. The identifications of these peaks are listed in Table 1 according to the peak number. This table also shows the structure of the compounds. The largest peak is intact NB (peak 6). Peaks 1, 5, 9, 12, and 15 are silanes, presumably originating from the column. Peak 8 is unknown, but with a molecular weight near 270, it is likely from the column as well. Peak 13 is butylated hydroxytoluene (BHT), which is an additive present in the ether. All other peaks are sonolytic breakdown products from NB.

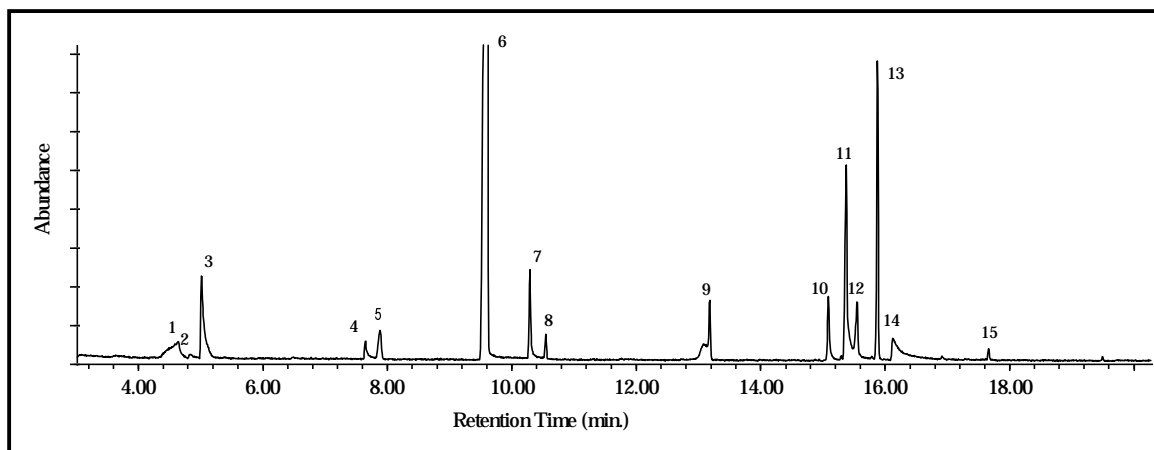
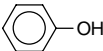
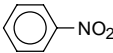
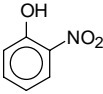
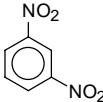
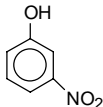



Figure 14. GC/MS trace of an ether extract of the treated NB solution after 40 hours of irradiation at 20 kHz.

Table 1. List of peak identifications and structures from the ether extract of the treated NB solution using 20 kHz irradiation. Numbers correspond to the peaks in Figure 14.

Peak Number	Ret. Time (min.)	Compound	Structure
1	4.63	Si compound	
2	4.84	4-methyl-3-pentenal	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{C}-\text{C}=\text{C}-\text{C} \\ \quad \quad \quad \text{CH}_3 \end{array}$
3	5.03	4-methyl-4-hydroxy-2-pentanone	$\begin{array}{c} \text{O} \quad \quad \text{OH} \\ \parallel \quad \quad \mid \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \quad \quad \quad \text{CH}_3 \end{array}$
4	7.65	phenol	
5	7.88	Si compound	
6	9.59	nitrobenzene	
7	10.29	2-nitrophenol	

Peak Number	Ret. Time (min.)	Compound	Structure
8	10.55	MW 270	
9	13.18	Si compound	
10	15.09	1,3-dinitrobenzene	
11	15.38	3-nitrophenol	
12	15.55	Si compound	
13	15.87	butylated hydroxytoluene	
14	16.13	4-nitrophenol	
15	17.66	Si compound	

A second extraction experiment was done using methylene chloride (MeCl) on a different aliquot of the same treated NB solution; Figure 15 shows its chromatogram. Based on this data, each solvent has its own advantages as an extraction solvent. For common organic compounds except 2-nitrophenol, the extraction efficiencies for the organic constituents are better in ether. More background silanes are removed from the column by MeCl and complicate the chromatogram at later retention times (not shown). Each extract's subset of components must then be combined to obtain the total set of sonolytic by-products. Table 2 identifies the numbered MeCl extracted peaks. Peaks 11 and 12 are column silanes but all other peaks are NB by-products. Peak 4 remains unidentified. Comparison of common species present in the ether extract and the MeCl extract shows excellent agreement for the retention times.

Discussion of NB sonolysis at 20 kHz

Table 3 lists proposed reactions that take place in this system based on the known reactions occurring during cavitation and the set of by-products from Tables 1 and 2. The primary reactions are those that occur in the bubble interior during cavitation. These reactions initiate formation of the radical species required for oxidation and reduction. Reaction 1 provides the hydrogen and hydroxyl radicals from the thermal breakdown of water vapor within the bubble. Reaction 3 requires the presence of NB within the bubble for pyrolytic breakdown. Pyrolysis is known to be a primary mechanism for sonolytic degradation. During sonolysis, it has been proposed that this mechanism will decompose NB to form the benzyl radical and NO_2 with further by-products created from this point (Kotronarou, Mills, and Hoffmann 1991).

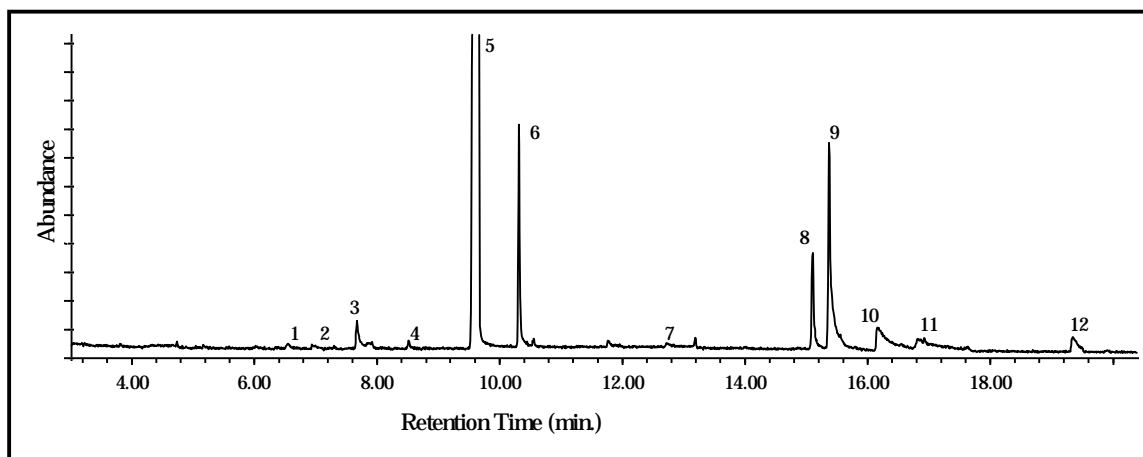


Figure 15. GC/MS trace of methylene chloride extract of the treated NB solution after 40 hours of irradiation at 20 kHz.

Table 2. List of peak identifications and structures from the methylene chloride extract of the treated NB solution using 20 kHz irradiation. Numbers correspond to the peaks in Figure 15.

Peak Number	Ret. Time (min.)	Compound	Structure
1	6.54	p-benzoquinone	<chem>O=C1C=CC(=O)C=C1</chem>
2	6.97	N,N-diethylformamide	<chem>CCN(CC)C=O</chem>

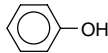
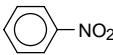
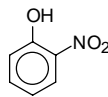

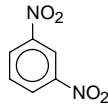
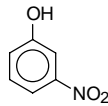
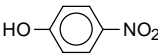














Peak Number	Ret. Time (min.)	Compound	Structure
3	7.69	phenol	
4	8.52	MW 124	
5	9.65	nitrobenzene	
6	10.30	2-nitrophenol	
7	12.73	2,3-dihydro-1H-indene-1-one	
8	15.10	1,3-dinitrobenzene	
9	15.38	3-nitrophenol	
10	16.17	4-nitrophenol	
11	16.84	Si compound	
12	19.35	Si compound	

Table 3. List of proposed reactions occurring during sonolysis of NB at 20 kHz.

<u>Primary Reactions</u>				
H_2O	\longrightarrow	H^\bullet	+	OH^\bullet (1)
O_2	\longrightarrow	2O		(2)
	\longrightarrow		+	NO_2^\bullet (3)
<u>Recombination and Termination Reactions</u>				
OH^\bullet	+	H^\bullet	\longrightarrow	H_2O (4)
H^\bullet	+	O_2	\longrightarrow	$\text{HO}_2^\bullet \longrightarrow \text{H}^+ + \text{O}_2^{\bullet -}$ (5)
2H^\bullet	\longrightarrow	H_2		(6)
2OH^\bullet	\longrightarrow	H_2O_2		(7)
H_2O_2	\longrightarrow	2OH^\bullet		(8)
<u>Secondary and Termination Reactions</u>				
	+	OH^\bullet	\longrightarrow	 + H^\bullet (9)
	+	H^\bullet	\longrightarrow	 + H_2 (10)
	+	OH^\bullet	\longrightarrow	 + H_2O (11)
	+	NO_2^\bullet	\longrightarrow	 (12)
	+	OH^\bullet	\longrightarrow	 + $\text{OH}^\bullet \longrightarrow$
				 \longrightarrow  (13)

The second regime includes the recombination and termination reactions. These occur later, and at a farther distance from the bubble interior. Reactions of this type are not useful for organic degradation. The major termination reaction is Reaction 4, which results in the reformation of water. It has been shown that the superoxide radical from Reaction 5, HO_2^\bullet , is required for the production of protein microspheres (Grinstaff and Suslick 1991) and may be an active radical species in these degradation reactions. Hydrogen peroxide, H_2O_2 , is actively generated in reaction 7, but may merely provide a source of hydroxyl radicals from further breakdown in reaction 8.

The final regime contains the secondary and termination reactions. These reactions produce the organic by-products that are detected by LC and GC/MS. Reaction 9 provides the pathway for production of the nitrophenols. The 2- and 3- isomers are more abundant than the 4- isomer based on peak intensities. these nitrophenols are the major by-product from sonolysis of NB.

Reactions 10 and 11 are two means of producing the nitrobenzyl radical. Further combination with the NO_2 radical (Reaction 3) results in the dinitrobenzene molecule (Reaction 12). GC/MS data indicates that only the 1,3-dinitrobenzene isomer is formed. The only other major pathway requires the hydroxyl radical attack on the benzyl radical from Reaction 3. Reaction 13 combines multiple reactions to produce first phenol, then dihydroxybenzene species. The amount of phenol produced is quite small and no dihydroxybenzene species are detected. However, p-benzoquinone is observed, presumably from the oxidation of hydroquinone.

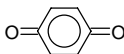
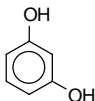

GC/MS analysis of neat ether and neat methylene chloride showed no spurious peaks due to impurities. Therefore, the additional species from Tables 1 and 2 are from the extracted NB solutions, but are difficult to explain. Specifically, 4-methyl-3-pentenal (peak 2) and 4-methyl-4-hydroxy-2-pentanone (peak 3) from Table 1 and N,N-diethylformamide (peak 2) and 2,3-dihydro-1H-indene-1-one (peak 7) from Table 2 are not typical products of sonolysis. These species have their origin from the breaking of the aromatic ring. Other studies show only small organic acids as precursors to CO_2 production.




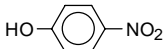
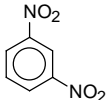
From the information gleaned from GC/MS data analysis, several of the identified by-products were studied by LC to determine their retention times. Table 4 lists the by-product followed by its structure, LC retention time, and if present, its most probable corresponding peak number from Figure 11. As mentioned above, a shift in chromatographic behavior over time makes clear assignment of the peak difficult in Figure 11. Benzoquinone is the only

unambiguous assignment at peak 3. The presence of phenol is recognized by GC/MS but the small shifting peaks in the LC trace near 5 minutes creates the possibility that phenol could be any of the peaks 6 through 9. The three nitrophenol isomers also shift noticeably; 2- and 3-nitrophenol tend to elute closely while 4-nitrophenol has a slightly longer retention time. Therefore, 2- and 3- nitrophenol are assigned to peaks 11 or 12 and 4-nitrophenol is assigned to either 12 or it co-elutes with NB. 1,3-Dinitrobenzene also co-elutes with NB. Resorcinol and catechol are two dihydroxybenzene compounds that might be expected from Reaction 13. Neither is observed by GC/MS and catechol is not seen at 3.1 minutes on the LC. Resorcinol, however, may be present as peak 4 in Figure 11 and poor solvent extraction could be the reason for its absence in GC/MS analysis.

Although no LC analysis was performed on the base water, the small rise in the TOC indicated that some useful information might result from GC/MS. An ether extraction was performed on the base water, concentrated and injected. Figure 16 shows the chromatographic trace of the ether extraction of the base water. Seven areas of interest are noted. Peak 5 is the ether inhibitor, butylated hydroxytoluene, and peaks 7 and 8 are phthalates most likely from the plastic bottle and tubing used in the system.

Table 4. Analysis of standards by LC. Compounds detected by GC/MS were analyzed by LC; the structure, retention time, and possible peak number in Figure 11 is listed. A value of NB in the Peak Number column indicates probable co-elution with nitrobenzene.

Compound	Structure	Ret. Time (min.)	Peak Number
Benzoquinone		2.3	3
Resorcinol		2.4	4 ?
Catechol		3.1	-

Compound	Structure	Ret. Time (min.)	Peak Number
Phenol		4.5 - 5.0	6 or 7
2-Nitrophenol		7.6	11 or 12
3-Nitrophenol		7.9	11 or 12
4-Nitrophenol		8.1	12 or NB
1,3-Dinitrobenzene		8.5	NB

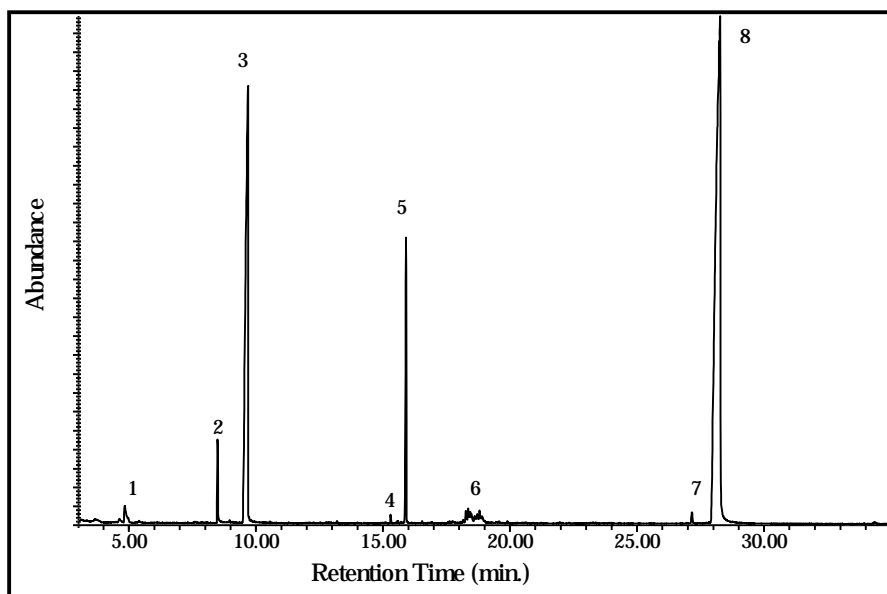


Figure 16. GC/MS trace of an ether extract of the base water after 40 hours of irradiation at 20 kHz.

As expected, the large NB peak (3) indicates that volatilization is a major concern. Peak 1 is a methyl pentenal compound similar to peak 2 in Table 1 providing corroboration of this species as a real by-product. The three remaining features are difficult to explain. Peak 2 is 2-ethylhexanol, peak 4 is a cyclohexadiene-dione compound and the peaks in area 6 are alkyl-substituted phenols. Although these three peaks provide reasonable peak matches from the MS library, the fact that none of these were also detected in the treated NB solution refutes the possibility that these are true sonolytic by-products. It is highly unlikely that these compounds would be completely sparged from the NB solution if they were continually produced as sonolytic intermediates.

Sonolysis of NB - 660 kHz

It is expected that the use of a higher frequency ultrasound source will increase the degradation rate of organic constituents in aqueous solutions. For example, it has been noted that the degradation of TNT is more efficient at 500 kHz than 20 kHz (Hoffmann, Hua, and Hochemer 1996). The higher frequency generates smaller bubbles with a shorter lifetime and thus permits more free-radical species to migrate into the solution before a recombination reaction (Petrier et al. 1994). Therefore, the fraction of free-radical degradation should increase versus pyrolysis at higher frequencies. Different sonolytic by-products or the by-product ratios can be expected to change.

Figure 17 shows the progression of LC data from the use of 660 kHz ultrasound. This figure also lists the irradiation times for each LC trace, and shows the initial LC trace for comparison. After an irradiation time of 116 minutes, the ultrasonic amplifier began to have periodic current faults — a condition that automatically turns off the system. Over time, these current faults became more frequent. (Immediately after this experiment, the unit was sent back for repair.) So, the true irradiation time for the upper trace on Figure 17 is not exactly known and is labeled as >137 minutes, with an upper bound of 158 minutes.

The LC traces show the growth of sonolytic by-products surrounding the large NB peak (peak 10). After only 6 minutes of irradiation, a substantial peak (peak 3) is seen at 2.3 minutes. As pointed out above (Table 4), this corresponds to p-benzoquinone. Peak 5 is the only other by-product noted. Unlike the 20 kHz system, no nitrophenols are produced at this point. After nearly 39 minutes of irradiation, additional peaks in regions 1 and 2 and peak 6 are observed. Peak 6 is most likely phenol while region 1 consists of organic ion peaks indicative of more complete breakdown of the NB. A very small amount of nitrophenol may be the origin of the peak near 8 minutes.

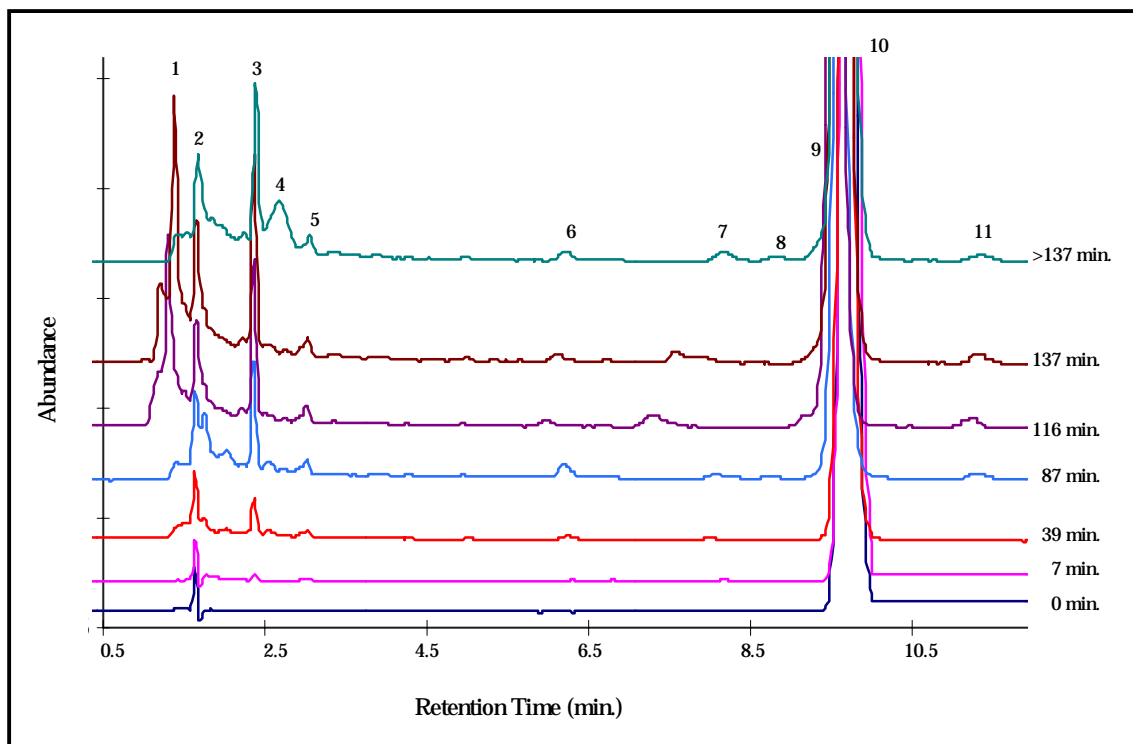


Figure 17. LC traces of the NB solution irradiated at 660 kHz taken at different experiment times. The irradiation time is noted near each trace and the initial NB solution is shown for comparison.

Further sonication continues these trends. After 87 minutes, peaks in region 2 become dominant, but benzoquinone remains the single largest by-product. The first appearance of peak 11 is also noted. At 116 minutes, the large peak in region 1 has appeared but it completely vanishes at >137 minutes. At later times, peaks 7, 8, and 9 may be the three nitrophenol isomers, and peak 11 may be a dinitrobenzene isomer.

An ether extraction was done on the sample treated > 137 minutes and the extract was analyzed by GC/MS. Figure 18 shows the chromatogram. The inset provides an expanded view of the crowded region between 15.5 and 18.5 minutes. Direct comparison with Figures 14 and 15 shows that treatment with the higher ultrasonic frequency produces a wider variety of by-products. Analysis of LC (Figure 17) is not sensitive enough to detect all of these species. Table 5 is a list of the best library matches for the numbered peaks in Figure 18, together with the retention time and the structure. NB (peak 7) dominates the trace as expected. The results confirm the identification of the LC peaks mentioned above and duplicate nearly all the peaks obtained by the use of 20 kHz ultrasound. The by-products will be explored further below in the discussion section for 660 kHz.

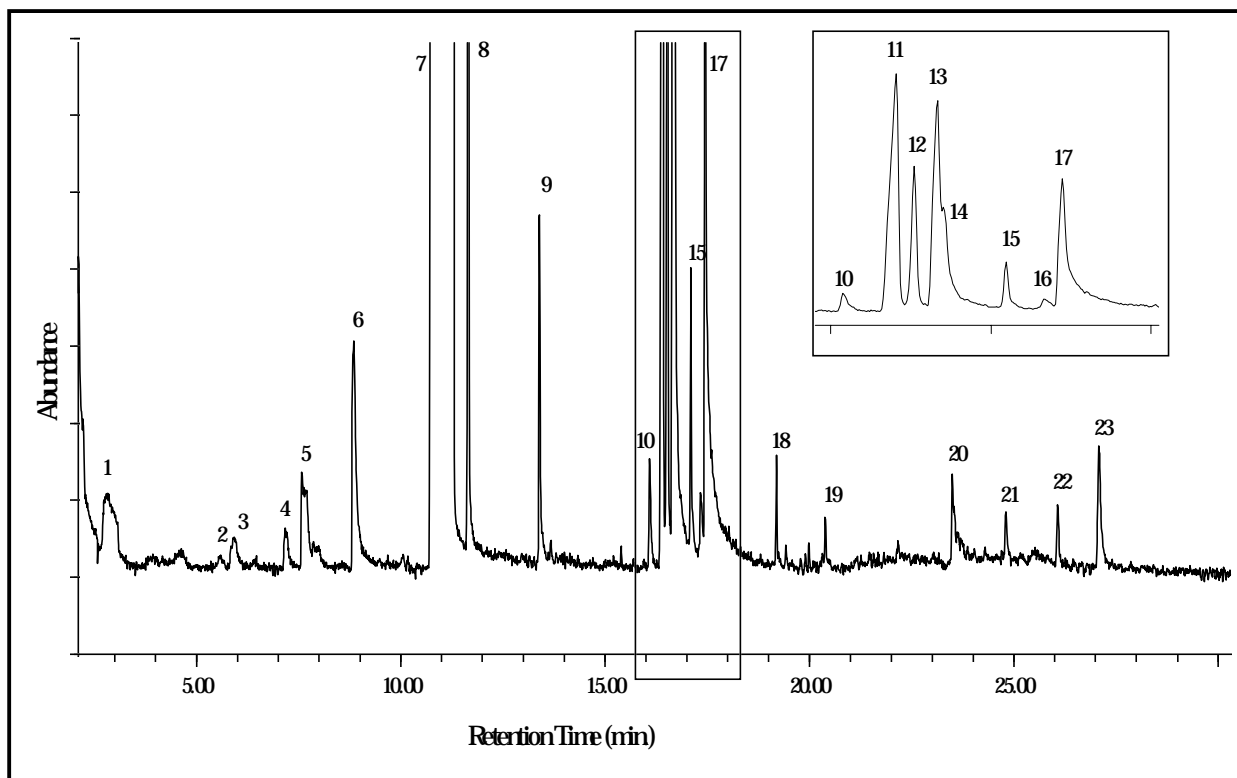

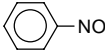
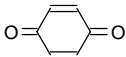
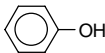
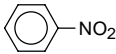
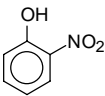
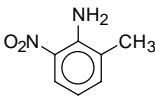
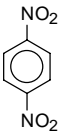
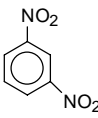
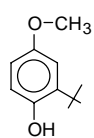
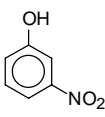
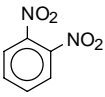



Figure 18. GC/MS trace of an ether extract of the treated NB solution after >120 minutes of irradiation at 660 kHz.

Table 5. List of peak identifications and structures from the ether extract of the treated NB solution using 660 kHz irradiation. The numbers correspond to the numbered peaks in Figure 18.

Peak Number	Ret. Time (min.)	Compound	Structure
1	2.78	benzene	
2	5.59	2,4-dimethylheptane	$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$
3	5.91	3-ethylpentene	$\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{CH}_2\text{CH}_3 \end{array}$
4	7.17	nitrosobenzene	
5	7.61	p-benzoquinone	

Peak Number	Ret. Time (min.)	Compound	Structure
6	8.84	phenol	
7	10.77	nitrobenzene	
8	11.68	2-nitrophenol	
9	13.38	2-methyl-6-nitroaniline	
10	16.08	1,4-dinitrobenzene	
11	16.39	1,3-dinitrobenzene	
12	16.52	3-tertbutyl-4-hydroxyanisole	
13	16.66	3-nitrophenol	
14	16.70	1,2-dinitrobenzene	
15	17.09	butylatedhydroxytoluene	
16	17.34	MW 155	
17	17.44	4-nitrophenol	

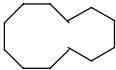
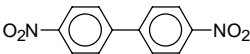
Peak Number	Ret. Time (min.)	Compound	Structure
18	19.19	cyclododecane	
19	20.38	Si compound	
20	23.51	Si compound	
21	24.82	Si compound	
22	26.81	Si compound	
23	27.09	4,4'-dinitro-1,1'-biphenyl	

Figure 19 shows the efficiency of the extraction process. The LC trace of the aqueous solution after ether extraction shows that ether performs well in the extraction of the late eluting, nonpolar by-products. Only a small peak remains beyond 4 minutes after extraction, which is likely residual NB. Based on this trace, the majority of benzoquinone is still in the aqueous fraction. None of the polar products near the injection peak are effectively removed. Clearly, these peaks must be identified by a different method.

Discussion of 660 kHz

Despite the presence of by-products and their growth throughout the irradiation period, the NB concentration does not decrease in any kind of orderly fashion. Peak area measurements for NB show a nearly cyclical trend with many samples having an NB concentration higher than the initial sample. This may be related to the difficulties in dissolving NB in water or NB losses during LC sample preparation. NB dissolution problems would lead to a nonhomogenous solution, which could show a random NB sample concentration. The agitation that occurs during sonication will enhance the NB dissolution process so it is not surprising to observe NB concentrations in treated solution higher than the measured initial NB concentration. After sample filtration, NB losses have been observed on the filter material.

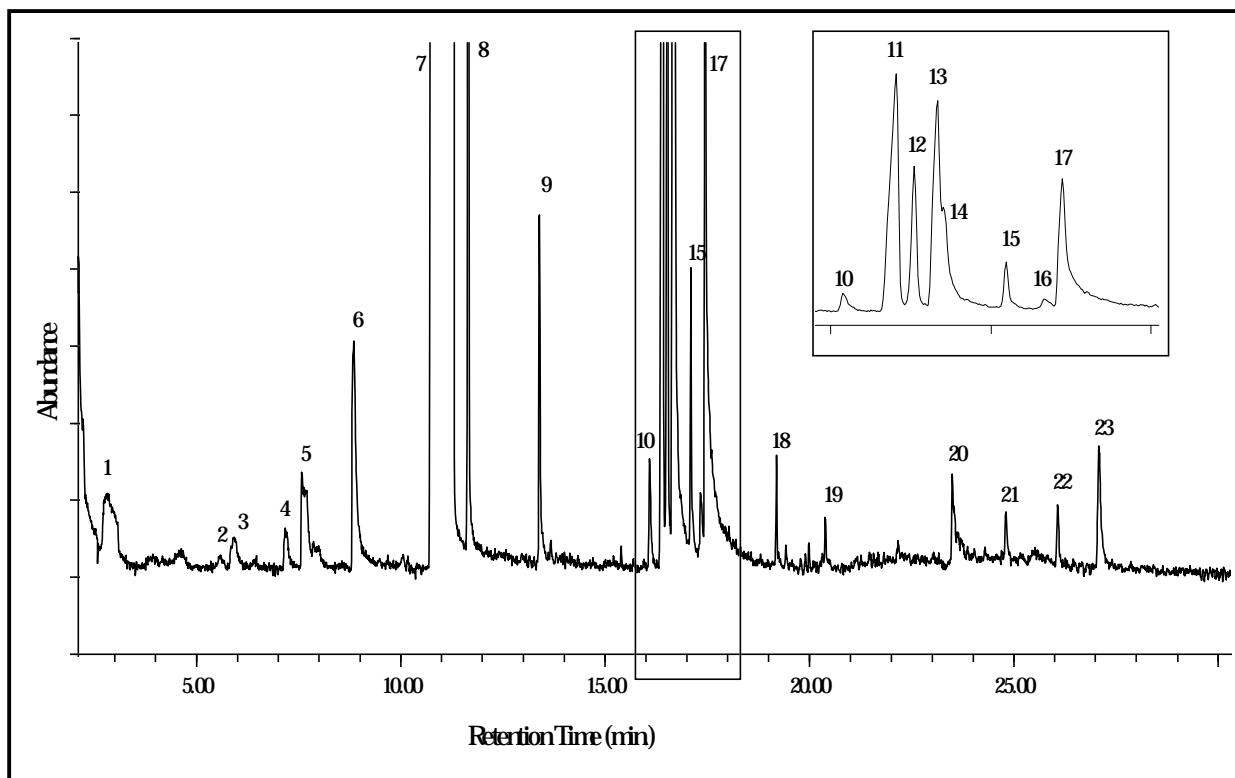


Figure 19. LC trace of the treated NB solution after ether extraction.

All the reactions presented in Table 3 are still applicable in this experiment. Reaction 3 is required to produce the NO_2 radical and the benzyl radical to take part in Reactions 12 and 13. Reaction 9 again results in the three nitrophenol isomers. The nitrobenzyl radical from either Reaction 10 or 11 is available to react with the NO_2 radical to produce dinitrobenzene (DNB) as shown in Reaction 12. In contrast to the experiment at 20 kHz, all three DNB isomers are produced with a relative ratio of 1,3-DNB > 1,2-DNB > 1,4-DNB. Reaction 13 results in the presence of both phenol and benzoquinone, but again, there was no evidence of any benzenediols, such as hydroquinone, catechol, or resorcinol.

Some new species were also produced. Figure 20 shows three additional reactions that can explain the formation mechanism of several of these compounds. The reactions discussed thus far do not require the presence of the hydrogen radical. It appears that use of 660 kHz increases the role of $\text{H}\cdot$. Reaction 14 shows the termination reaction between the benzyl radical and $\text{H}\cdot$ to form benzene (peak 1). Reaction 15 illustrates the reduction of the nitro group to form nitrosobenzene (peak 4). Continuation of Reaction 15 would produce aniline, but this compound was not observed; however, 2-methyl-6-nitroaniline (peak 9) was produced. This species also implies that methyl or methylene radicals are present from breakdown of the aromatic ring of NB. Long chain hydrocarbons (peaks 2 and 3) would originate from the aromatic ring as well. 3-Tertbutyl-4-hydroxyanisole (peak 12) and cyclododecane (peak 18) indicate the

presence of more complex carbon radicals. Peak 16 remains unknown with a molecular weight of 155. The final detected by-product is unique, resulting from the dimerization of NB. This 4,4'-dinitro-1,1'-biphenyl compound is the first case of dimerization observed in this work. Reaction 16 shows one possible origin for the dinitrobiphenyl compound.

Since standards of this compound and other dinitrobiphenyl isomers were not available for matching retention time and mass spectra, definitive confirmation of peak 23 as the 4,4'-dinitro species was not achieved. Because of the multiple possible pathways for reactions of the nitrophenyl radical, it is difficult to comment on the relative abundances of the three possible radical positions, ortho, meta, or para. The appearance of only the 4,4'-dinitro isomer may imply either the dominant production of the nitrophenyl radical in the para position, or that steric effects prevent the combination of meta or ortho radicals, leaving them available for participation in Reaction 12 while the para radicals are consumed by Reaction 16. The presence of the biphenyl compound as well as the increased appearance of all three DNB isomers emphasizes the importance of Reactions 10 and 11 at 660 kHz over their occurrence at 20 kHz.

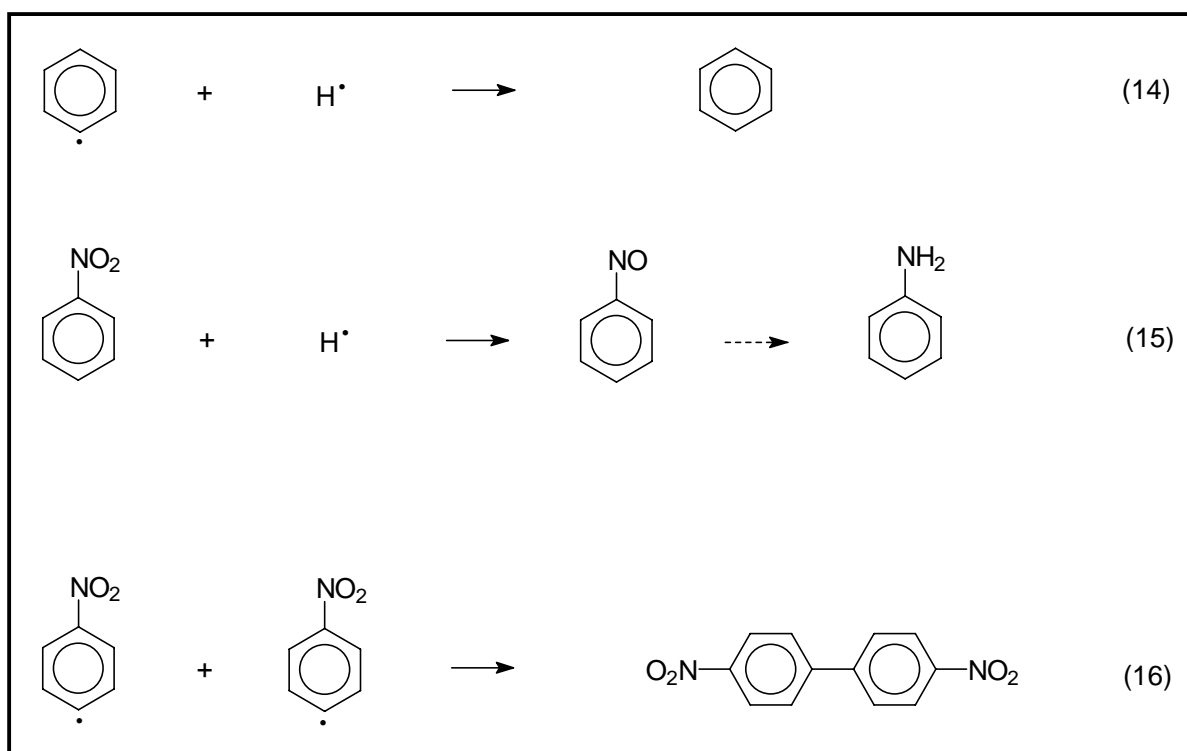


Figure 20. Several additional reactions occurring during sonolysis of NB at 660 kHz.

As a final note, the results obtained by sonolytic destruction can be compared to results obtained by photocatalytic degradation of NB. In photocatalysis, if light of sufficient energy impinges upon a semiconductor surface, an electron is elevated to the conduction band, leaving a hole in the valence band. When the semiconductor is in water with an organic contaminant, several reactions can occur at the semiconductor surface. First, water may react with the hole to produce a hydroxyl radical. Second, the organic species may react with the hole to become oxidized. Third, the organic species may react with the excited electron to become reduced. With the potential of observing both oxidation and reduction reactions, photocatalytic reactions show many similarities to sonolytic reactions.

Photocatalysis on NB has shown that the three nitrophenol isomers are approximately equally produced (D'Oliveira et al. 1993). Other reports, however, have a more extensive by-product listing. Maillard et al. (1994) has uncovered the following species: the three nitrophenol isomers, nitrohydroquinone, benzoquinone, phenol, nitrosobenzene, all three DNB isomers, acetate, and formate, but did not find hydroquinone or any dihydroxynitrophenol compounds. These results are quite similar to the results obtained with the 660 kHz sonicator. In fact, the appearance of nitrohydroquinone in photocatalysis provides a possible clue to the unknown species in Table 5 (peak 16 in Figure 18). This unknown compound has the mass spectrum shown in Figure 21. The large mass peak at $m/z = 155$ are assumed to be the molecular weight peak. The structure of nitrohydroquinone is shown in the inset of Figure 21. Loss of either -OH fragment would give the $m/z = 138$ peak, the loss of -NO would give the $m/z = 125$ peak, and the loss of -NO₂ would give the $m/z = 109$ peak. Preliminary analysis would thus support the assignment of this peak as nitrohydroquinone.

Experience with other nitro compounds, however, weakens any argument since Figure 21 does not possess any prominent mass peak at $m/z = 30$ or 46 due to the -NO and -NO₂ fragments, respectively. An unambiguous conclusion requires obtaining a sample of nitrohydroquinone and matching both retention behavior and mass spectral data. Another study on photocatalysis of NB also detected the three nitrophenol isomers, phenol, ammonium ion, and nitrate as by-products, but did not find nitrosobenzene and or (Minero et al. 1994). Interestingly, this work also observed dimerization of NB to provide precedence for this process in oxidizing/reducing environments.

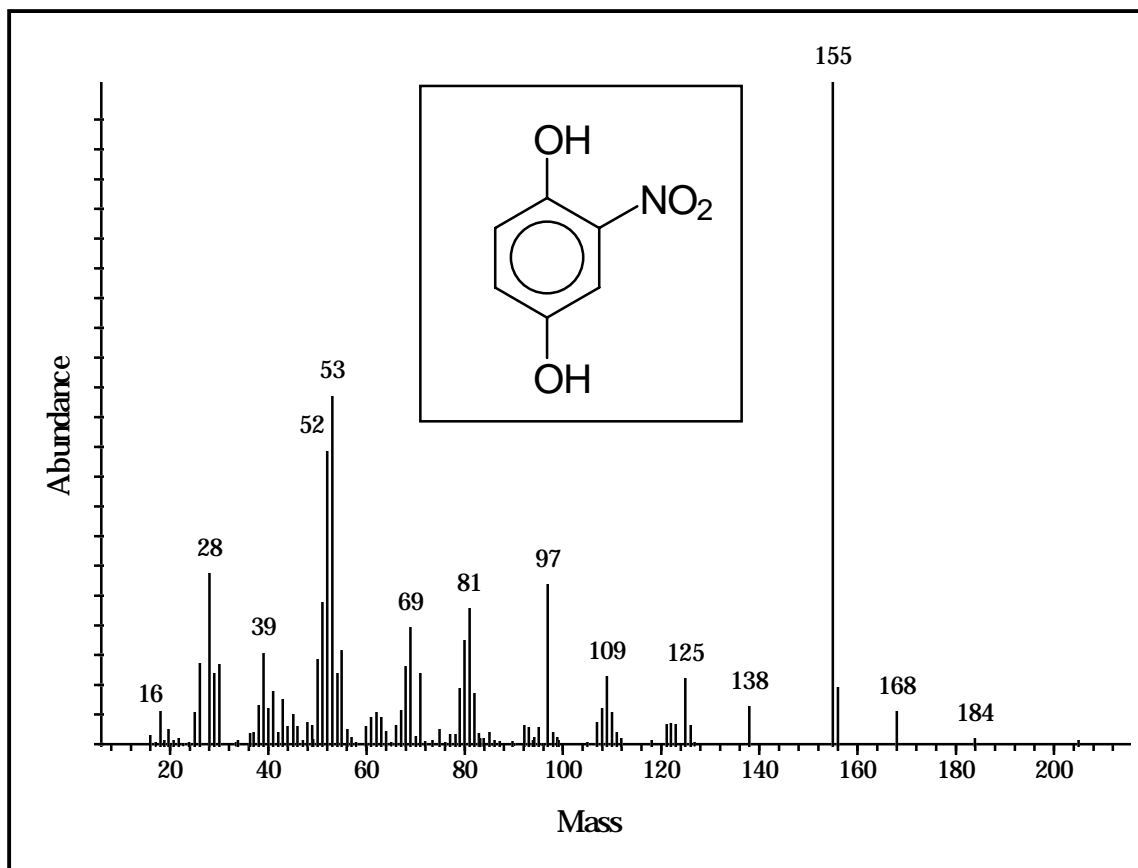


Figure 21. Mass spectrum of the unknown by-product (peak 16 in figure 18) produced by irradiation at 660 kHz. The inset shows the structure of nitrohydroquinone (MW = 155), which is an identified by-product of photochemical degradation of NB.

Future Work

Future work in sonolysis of nitrocompounds will study the effects of different experimental parameters on the kinetics and mechanism of destruction. First, the effects of solution temperature will be studied. Maximum cavitation occurs in water at 35 °C (Soudagar and Samant 1995) and it is expected that this would also increase the degradation rate. Conversely, for some processes, increasing the temperature actually decreased the rate (Lorimer et al. 1995). Lack of a prominent temperature effect would save the energy of heating or cooling the solution in full scale treatment systems. Second, the effect of sparge gas will be studied. Use of noble gases increases the cavitation temperature due to both a decrease in the kinetic degrees of freedom of the gas molecule where energy can be lost, and a lower thermal conductivity, which prevents heat from dissipating from the bubble (Hoffmann, Hua, and Hochemer 1996). The final main experimental parameter is the ultrasonic frequency. An additional instrument that is capable of irradiation at 360 kHz and 1.07 MHz is now available for use.

Additional capabilities will be employed to help in problem areas, primarily the identification of unknown products. CERL now has several new instruments and devices that will further the analysis of treated solutions. A Varian Saturn 2000 GC/MS now on-site is at least an order of magnitude more sensitive than the Hewlett-Packard instrument used in this experiment, and it can perform chemical ionization as well as tandem mass spectrometry for structure elucidation. A Finnegan LCQ with electrospray ionization has been installed as a detector for LC analysis to provide mass spectral analysis on analytes that remain in the aqueous phase. Finally, an ion exchange column with a conductivity detector is available for analysis of inorganic ions such as nitrate and nitrite, and organic ions such as acetate, formate, and gluconate.

An important area of additional work will address the problem of volatility. Clearly, the base water used in these experiments is not an optimal accumulation solvent for any organic species that escape from the treatment vessel. Instead, solid sorbent traps will be used between the solution vessel and the base water vessel. These can then be analyzed by thermal desorption GC/MS. It would be preferable, however, to eliminate the volatility problem. Investigations into the use of additives to keep the organic in solution will be performed. A small amount of solvent added to the system may keep the substrate in the active sonolysis zone. Surfactant will also be extensively studied as an agent for increasing the organic solubility. Formation of micelles can provide a desirable environment for the contaminant until destruction.

4 Conclusions

This study concludes that DNB is more resistant to sonolysis than NB. Since the production of by-products does not track the disappearance of DNB, volatility is the primary mode of DNB loss. The poor solvation of DNB by water as well as the large solution surface area allows rapid volatility. Since NB is more soluble in water, it remains available for sonolysis longer and produces a wider variety of by-products than sonolysis of DNB. Therefore, organic compounds that are less soluble in water will be more difficult to effectively treat by sonolysis unless steps are taken to increase the presence of the contaminant in the irradiation zone. It is also noted that a higher irradiation frequency is more efficient at sonolysis. More intermediates are observed at shorter irradiation times than with a lower ultrasonic frequency. In addition, a different subset of intermediates are formed, indicating alternate sonolytic pathways are followed. Further work will continue on other nitroaromatic species such as nitrotoluenes, dinitrotoluenes, and trinitrotoluene.

The work performed on DNB and NB illustrates two main problems with the use of ultrasound for contaminant degradation. First, under the experimental conditions used here, the process is slow. Although this work does not emphasize maximizing the degradation rate, the fate of future applied research may rest in the ability to show favorable comparisons to other treatment processes in terms of both cost and efficiency. Second, as mentioned above, the agitation produced by ultrasonic irradiation initiates more volatilization than degradation. Nevertheless, these experiments show the ability of high-intensity sound waves to degrade nitroaromatic species in water.

References

- Kotronarou, A., G. Mills, and M.R. Hoffmann, "Ultrasonic Irradiation of p-Nitrophenol in Aqueous Solution," *J. Phys. Chem.*, vol 95 (1991), p 3630.
- Berlan, J., F. Trabelsi, H. Delmas, A.M. Wilhelm, and J.F. Petrignani, "Oxidative Degradation of Phenol in Aqueous Media Using Ultrasound," *Ultrasonics Sonochemistry*, vol 1 (1994), p S97.
- Bremner, D., "Historical Introduction to Sonochemistry," in *Advances in Sonochemistry*, T.J. Mason, ed., vol 1 (JAI Press Ltd., Greenwich, CT, 1990), p 1.
- Cheung, H.M., A. Bhatnagar, and G. Jansen, "Sonochemical Destruction of Chlorinated Hydrocarbons in Dilute Aqueous Solution," *Env. Sci. Tech.*, vol 25 (1991), p 1510.
- Code of Federal Regulations, 40, pt 260–299, sec 261.32 (Washington, DC, 1 July 1996).
- D'Oliveira, J., C. Guillard, C. Maillard, and P. Pichat, "Photocatalytic Destruction of Hazardous Chlorine- or Nitrogen-Containing Aromatics in Water," *J. Env. Sci. Health*, vol a28, No. 4 (1993), p 941.
- Dean, J.A., ed., *Lange's Handbook of Chemistry*, 13th ed. (McGraw Hill, NY, 1972).
- Drijvers, D., R. De Baets, A. De Visscher, and H. Van Langenhove, "Sonolysis of Trichloroethylene in Aqueous Solution: Volatile Organic Intermediates," *Ultrasonics Sonochemistry*, vol 3 (1996), p S83.
- Francony, A., and C. Petrier, "Sonochemical Degradation of Carbon Tetrachloride in Aqueous Solution at Two Frequencies: 20 kHz and 500 kHz," *Ultrasonics Sonochemistry*, vol 3 (1996), p S77.
- Fuchs, E., and H. Heusinger, "Sonolysis and Radiolysis of Glyceraldehyde in Deaerated Aqueous Solution," *Ultrasonics Sonochemistry*, vol 2 (1995), p S105.
- Grinstaff, M.W., and K.S. Suslick, "Air-Filled Proteinaceous Microbubbles: Synthesis of an Echo-Contrast Agent," *Proceedings of the National Academy of Science USA*, vol 88 (1991), p 7708.
- Gutierrez, M., A. Henglein, and F. Ibanez, "Radical Scavenging in the Sonolysis of Aqueous Solutions of I, Br, and N₃," *J. Phys. Chem.*, vol 95 (1991), p 6044.
- Harradine, D.M., S.J. Buelow, P.C. Dell'orco, R.B. Dyer, B.R. Foy, J.M. Robinson, J.A. Sanchez, T. Spontarelli, and J.D. Wander, "Oxidation Chemistry of Energetic Materials in Supercritical Water," *Haz. Waste and Haz. Materials*, vol 10 (1993), p 233.
- Hirai, K., Y. Nagata, and Y. Maeda, "Decomposition of Chlorofluorocarbons and Hydrofluorocarbons in Water by Ultrasonic Irradiation," *Ultrasonics Sonochemistry*, vol 3 (1996), p S205.

- Hoffmann, M.R., I. Hua, and R. Hochemer, "Application of Ultrasonic Irradiation for the Degradation of Chemical Contaminants in Water," *Ultrasonics Sonochemistry*, vol 2 (1996), p S163.
- Lorimer, J.P., T.J. Mason, T.C. Cuthbert, and E.A. Brookfield, "Effect of Ultrasound on the Degradation of Aqueous Native Dextran," *Ultrasonics Sonochemistry*, vol 2 (1995), p S55.
- Luche, J.L., "Ultrasonically Promoted Carbonyl Addition Reactions," in *Advances in Sonochemistry*, T.J. Mason, ed., vol 1 (JAI Press Ltd., Greenwich, CT, 1990).
- Maillard-Dupuy, C., C. Guillard, and P. Pichat, "The Degradation of Nitrobenzene in Water by Photocatalysis Over TiO_2 : Kinetics and Products; Simultaneous Elimination of Benzamide or Phenol or Pb^{+2} Cations," *New J. Chem*, vol 18 (1994), p 941.
- Maloney, S.W., E.R. May, M.T. Suidan, S.R. Berchtold, and S. VanderLoop, *Treating Dinitrotoluene in Propellant Wastewater Using Anaerobic Fluidized-Bed Bioreactors Containing Granular Activated Carbon (GAC)*, Technical Report (TR) EP-95/07/ADA294387 (U.S. Army Construction Engineering Research Laboratories [CERL], March 1995).
- Mason, T., and J. Lorimer, *Sonochemistry: Theory, Applications, and Uses of Ultrasound in Chemistry* (Ellis Norwood, NY, 1988).
- Mason, T.J., A. Newman, J.P. Lorimer, J. Lindley, and K. Hutt, "Ultrasonically Assisted Catalytic Decomposition of Aqueous Sodium Hypochlorite," *Ultrasonics Sonochemistry*, vol 3 (1996), p 53.
- Minero, C., E. Pelizzetti, P. Piccinini, and M. Vincenti, "Photocatalyzed Transformation of Nitrobenzene on TiO_2 and ZnO ," *Chemosphere*, vol 28 (1994), p 1229.
- Petrier, C., D. Reyman, and J.L. Luche, "b-Carboline as a Probe for the Sonolysis of Alcohols and Chloromethanes," *Ultrasonics Sonochemistry*, vol 2 (1995), p S103.
- Petrier, C., M. Micolle, G. Merlin, J.L. Luche, and G. Reverdy, "Characteristics of Pentachlorophenate Degradation in Aqueous Solution by Means of Ultrasound," *Env. Sci. Tech.*, vol 26 (1992), p 1639.
- Petrier, C., M.F. Lamy, A. Francony, A. Benahcene, B. David, V. Renaudin, and N. Gondrexon, "Sonochemical Degradation of Phenol in Dilute Aqueous Solutions: Comparison of the Reaction Rates at 20 and 487 kHz," *J. Phys. Chem.*, vol 98 (1994), p 10514.
- Serpone, N., R. Terzian, H. Hidaka, and E. Pelizzetti, "Ultrasonic Induced Dehalogenation and Oxidation of 2-, 3-, and 4-Chlorophenol in Air-Equilibrated Aqueous Media. Similarities with Irradiated Semiconductor Particulates," *J. Phys. Chem.*, vol 98 (1994), p 2634.
- Serpone, N., R. Terzian, P. Colarusso, C. Minero, E. Pelizzetti, and H. Hidaka, "Sonochemical Oxidation of Phenol and Three of its Intermediate Products in Aqueous Media: Catechol, Hydroquinone, and Benzoquinone. Kinetic and Mechanistic Aspects," *Res. on Chem. Intermediates*, vol 18 (1982), p 183.
- Soudagar, S.R., and S.D. Samant, "Investigation of Ultrasound Catalyzed Oxidation of Arylalkanes Using Aqueous Potassium Permanganate," *Ultrasonics Sonochemistry*, vol 2 (1995), p S15.
- Suslick, K.S., "Sonochemistry," *Science*, vol 247 (1990), p 1439.

- Suslick, K.S., "The Chemical Effects of Ultrasound," *Scientific American* (1989), p 80.
- Suslick, K.S., and D.A. Hammerton, "The Site of Sonochemical Reactions," *IEEE Trans. Ultrasonic Ferroelec. Freq. Contr.*, vol 33 (1986), p 143.
- Suslick, K.S., and D.J. Casadonte, "Heterogeneous Sonocatalysis with Nickel Powder," *J. Amer. Chem. Soc.*, vol 109 (1987), p 3459.
- Suslick, K.S., R.E. Cline, Jr., and D.A. Hammerton, "The Sonochemical Hot Spot," *J. Amer. Chem. Soc.*, vol 108 (1986), p 5641.
- Suslick, K.S., S.B. Choe, A.A. Cichowlas, and M.W. Grinstaff, "Sonochemical Synthesis of Amorphous Iron," *Nature*, vol 353 (1991), p 414.
- Takizawa, Y., M. Akama, N. Yoshihara, O. Nojima, K. Aarai, and S. Okouchi, "Hydroxylation of Phenolic Compounds Under the Condition of Ultrasound in Aqueous Solution," *Ultrasonics Sonochemistry*, vol 3 (1996), p S201.
- Yinon, J., and S. Zitrin, *Modern Methods and Applications in Analysis of Explosives* (Wiley, NY, 1993).